**Solvent Co-Intercalation into Few-Layered Ti3C2T*x* MXenes in Lithium Ion Batteries Induced by Acidic or Basic Post-Treatment**

*Peer Bärmann1, Roman Nölle1, VassilIios Siozios1, Mirco Ruttert1, Olivier Guillon2,3,*

*Martin Winter1,4, Jesus Gonzalez‑Julian2,\*, Tobias Placke1,\**

1 University of Münster, MEET Battery Research Center, Institute of Physical Chemistry,

Corrensstr. 46, 48149 Münster, Germany

2 Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research: Materials Synthesis and Processing (IEK-1), Wilhelm-Johnen-Straße, 52425 Jülich, Germany

3 Jülich Aachen Research Alliance JARA, 52425 Jülich, Germany

4 Helmholtz Institute Münster, IEK-12, Forschungszentrum Jülich GmbH,

Corrensstr. 46, 48149 Münster, Germany

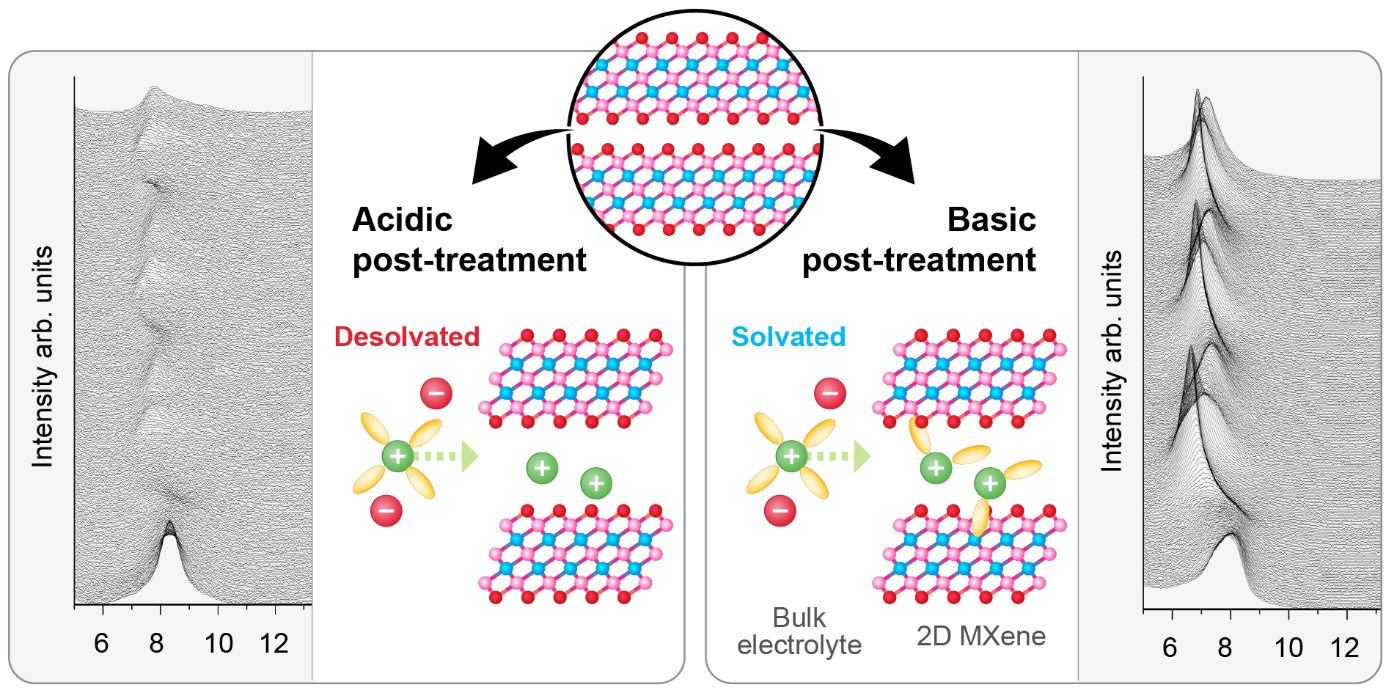
\*Corresponding authors: [tobias.placke@uni-muenster.de](mailto:tobias.placke@uni-muenster.de) (T.P.), j.gonzalez@fz-juelich.de (J.G.-J.)

**Abstract**

MXenes, as an emerging class of 2D materials, display distinctive physical and chemical properties, which are highly suitable for high-power battery applications, such as lithium ion batteries (LIBs). Ti3C2*Tx* (*Tx* = O, OH, F, Cl) is one of the most investigated MXenes to this day, however, most scientific research studies only focus on the design of multi-layered or mono-layer MXenes. Here, we present a comprehensive study on the synthesis of few‑layered Ti3C2*Tx* materials and their use in LIB cells, in particular for high-rate applications. The synthesized Ti3C2*Tx* MXenes are characterized *via* complementary XRD, Raman spectroscopy, XPS, EDX, SEM, TGA and nitrogen adsorption techniques to clarify the structural and chemical changes, especially regarding the surface groups and intercalated cations/water molecules. The structural changes are correlated with respect to the acidic and basic post‑treatment of Ti3C2*Tx*. Furthermore, the detected alterations are put into an electrochemical perspective *via* galvanostatic and potentiostatic investigations to study the pseudocapacitive behavior of few-layered Ti3C2*Tx*, exhibiting a stable capacity of 155 mAh g‑1 for 1000 cycles at 5 A g-1. The acidic treatment of Ti3C2T*x* synthesized *via* the *in-situ* formation of HF through LiF/HCl is able to increase the initial capacity in comparison to the pristine or basic treatment. To gain further insights into the structural changes occurring during (de)lithiation, *in-situ* XRD is applied for LIB cells in a voltage range from 0.01 to 3 V to give fundamental mechanistic insights into the structural changes occurring during the first cycles. Thereby, the increased initial capacity observed for acidic treated MXenes can be explained by the reduced co-intercalation of solvent molecules.

**KEYWORDS:** MXenes; MAX phases; lithium ion battery; *in-situ* XRD; Ti3C2T*x*

**Graphical abstract (TOC)**

****

**Introduction**

Since their discovery in 2011, the understanding of the chemical and physical properties of 2D layered transition metal carbides and nitrides (=MXenes) has grown rapidly. For synthesis of MXenes, MAX phases are generally used as the precursor material, consisting of an early transition metal (*M*), a group IV element (*A*) and carbon and/or nitrogen (*X*) in a fixed stoichiometry of n=1, 2, or 3 for *Mn*+1*AXn* (*e.g.*, Ti3AlC2). One of the most studied MXenes is Ti3C2*Tx* (*Tx* = O, OH, F, Cl; theoretically *x*=2). Here, *Tx* describes the surface termination groups, which substitute the “*A*” element of the MAX phases during the etching process to synthesize MXenes. The titanium-based MXene is one of the most studied ones to date, due to its high oxidative stability, high electronic and ionic conductivity and versatile activity towards different cations, such as Li+ and Na+.[1-3](#_ENREF_1)

Variations in the preparation and post‑treatment of MXenes can result in significantly different particle characteristics, such as particle morphology, particle size and surface group chemistry. MXenes can be prepared in form of a multi-layered, few-layered or single/mono-layered particles/sheets, depending on the precursor material, etching procedure and subsequent washing and/or post‑treatment (calcination, acid washing, *etc*.). Furthermore, the surface group chemistry (amount and type of surface groups) can be adjusted through an etching method or post-treatment and also plays a major role for the performance as negative electrode (=anode) in lithium ion battery (LIB) cells. Theoretically, oxygen-terminated surface groups are preferred due to the higher, expected capacity of 268 mAh g-1 in comparison to fluorine-terminated groups, which exhibit a theoretical capacity of 130 mAh g-1. [1](#_ENREF_1), [3-8](#_ENREF_3)

Up to date, MXenes have mainly been investigated in form of the multi-layered particles or single-layered MXenes for various electrochemical storage devices, such as LIBs, sodium-ion batteries or supercapacitors. [9-12](#_ENREF_9) Multi-layered particles usually display large particle sizes which limit their electrochemical rate performance and, therefore, display low reversible specific capacities at higher rates. Pure mono- or bi-layered MXenes display an excellent rate performance with high capacities of up to 420 mAh g-1 in organic electrolytes and can even be used as free-standing electrodes. Nevertheless, the monolayers are prone to severe oxidation and the high specific surface area typically results in a low Coulombic efficiency (*C*Eff). [13-19](#_ENREF_13)

In this work, few-layered Ti3C2*Tx* MXenes were synthesized and investigated for the application as anode material in LIB cells. The synthesized Ti3C2*Tx* were comprehensively characterized *via* X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM), nitrogen absorption analysis and thermogravimetric analysis (TGA) in order to systematically evaluate the impact of the synthesis route on the material properties. [8](#_ENREF_8) This extensive study is not only motivated by the precursor/etching route but also by the latest finding of the role of the intercalated lithium and the steric chloride termination for LiF/HCl etched MXenes. The chlorine termination leads to a more open interspace layer and, therefore, increases the Li+ accessibility of the redox active sites with less diffusion limitations, resulting in higher specific capacities. [20-22](#_ENREF_20)

The material characterization is put into an electrochemical perspective *via* galvanostatic and potentiostatic investigations, demonstrating the high rate capability of the synthesized few-layered MXenes, driven by the pseudocapacitive behavior. Finally, the structural changes of MXenes are investigated using *in-situ* XRD for LIB applications with an organic electrolyte in the full voltage range (0.01-3 V). By combination of various complementary analytical and electrochemical techniques, we are able to give fundamental insights into structure-performance relationships and point out the importance of various processing steps in the MXene preparation.

In summary, we aim to answer three distinctive questions to derive an improved fundamental understanding on the implications of acidic or basic post-treatment on the electrochemical behavior of titanium-based MXenes as anode materials for LIB cells: Firstly, we want to answer if there are significant structural or chemical composition changes induced by the post-treatment of few-layered MXenes. Secondly, we want to elucidate if these changes correlate to a change in the electrochemical behavior, especially with regard to the diffusion and non-diffusion limited processes (pseudocapacitive behavior). Thirdly, we want to clarify if the changes in electrochemical performance are induced by structural changes of the active material.

**Results and discussion**

The precursor material for MXene synthesis, *i.e.*, Ti3AlC2 (MAX phase), was synthesized from its elemental constituents by solid-liquid state reaction at high temperature and the different Ti3C2*Tx* materials were synthesized as described in the *supporting information*. An overview of all samples can be found in **Table S1**. Only the samples ‘Ti3C2‑pristine‑250C’ (dried at 250 °C), ‘Ti3C2-HCl‑250C’ (washed with 6M HCl and dried at 250 °C) and ‘Ti3C2‑LiOH‑250C’ (treated with LiOH and dried at 250 °C) are discussed in this paper. A comprehensive discussion for the other samples can be found in the *supporting information*.

X-ray diffraction can be used to qualitatively confirm the successful removal of the Al‑layer from the MAX phase Ti3AlC2. Generally, the (002) reflection corresponding to the basal planes of the Ti3AlC2 shifts to lower 2θ values if the etching procedure is successful. Furthermore, the reflection shift is mainly influenced by the formation of interstitial states of intercalated water molecules during the synthesis. Formation of bi-layers as well as monolayers of water is possible corresponding to interlayer distances ranging from 25 to 33 Å, respectively. Moreover, if intercalated cations (*e.g.,* Li+, K+) are present during the synthesis or post-treatment, the hydration energy of the cation plays a significant role in the intercalation process of water and results in clay‑like swelling of the MXene. The swelling is countered by the electrostatic attraction between the positively charged cations and the negatively charged Ti3C2*Tx* sheets, which in turn changes the interlayer distances. In addition to the cations, absorbed anions (*e.g.,* Cl-) at the positively charges edges of the MXenes as well as surface functional groups can have a steric effect on the intercalation process of water and probably other polar, protic solvents. [20-26](#_ENREF_20) Nevertheless, the following discussion will focus only on the samples dried at 250 °C. A more detailed discussion can be found in the *supporting information.*

As depicted in **Figure 1a**, all investigated samples display a clear shift from the theoretical (002) reflection of Ti3AlC2 from 9.50° towards lower 2θ values, indicating the successful synthesis of the MXene (PDF 00-052-0875). Clearly, a shoulder towards lower angles can be observed for Ti3C2-pristine-250C, which is due to the intercalation of water molecules. A detailed analysis and discussion can be found in the *supporting information* (see **Figure S1**, **S3** and **S4**).

As depicted in **Figure S1** and **S2**, all investigated samples display two distinctive crystalline reflections located at 36.2° and 42.0° between two broad reflections (shifted (010) and (012) from Ti3AlC2) at 35° and 43°. These reflections are most-likely the (103) and (106) reflections from the precursor Ti3AlC2, indicating few-layered Ti3C2*Tx*. Nevertheless, possible overlapping with impurities resulting from titanium carbide (TiC) cannot be ruled out as the phase is typically present in the precursor (PDF 01-071-0298). No distinctive TiO2 reflections from the anatase or rutile phase are present, indicating a minor or even no oxidation during the etching procedure (PDF 04-014-5794, PDF 04-014-0245). However, as these reflections also overlap with the shifted (004) and (008) reflections from Ti3C2*Tx*, Raman spectroscopy analysis is necessary to confirm these indications, which will be discussed later. Furthermore, a broad and small reflection, corresponding to LiF can observed at 38.9° and 45.0° (PDF 04-012-7777) especially for Ti3C2-pristine-250C, requiring the additional acidic washing step to remove these impurities (see also **Figure S12**). Washing of the few-layered MXenes with 6M HCl clearly led to the complete removal of the later mentioned reflections associated with LiF (Ti3C2-HCl in **Figure S2**).

To further investigate the oxidation and, therefore, the quality of the 2D Ti3C2*Tx* material, Raman spectroscopy was conducted, which also allows for a qualitatively description of the present surface groups. *Hu* *et al.* firstly described the Raman characteristics of Ti3C2*Tx* MXenes theoretically as well as experimentally, therefore, the reported assignment of the corresponding modes (ω1 to ω7) is also used in their work. [27](#_ENREF_27) Recently, the understanding of Raman spectra of Ti3C2*Tx* was expanded by *Lioi* *et al.,* as they discovered the resonance Raman scattering of MXenes, which led to the possibility of differentiating the different surface groups applied by different etching methods. [28](#_ENREF_28)

****

**Figure 1. (**a) X-ray diffraction patterns for Ti3C2-pristine-250C, Ti3C2-HCl-250C and Ti3C2-LiOH-250C in the 2θ range of 10° to 80°. The theoretical reflections discussed in the manuscript are labeled accordingly and marked by straight lines at the bottom. (b) Raman spectra for Ti3C2-pristine-250C, Ti3C2-HCl-250C and Ti3C2-LiOH-250C. The theoretical modes from *Hu et al.* are labeled accordingly and marked by straight lines. [31]

The Raman spectra of the three different samples can be observed in **Figure 1b**, while **Figure S5a** shows the full spectra and **Figure S5b** depicts only the ω3 mode of all investigated samples. The theoretically calculated modes for the terminated Ti3C2*Tx* are marked and shown at the bottom. [27](#_ENREF_27) First and foremost, no modes of TiO2 can be observed, clearly visible by the absence of the B1g mode at 143 cm-1. [29](#_ENREF_29) Furthermore, as shown in the full spectra in **Figure S6**, no D- or G-modes are visible for any of the samples (1200 to 1600 cm-1). [30-31](#_ENREF_30) Therefore, the results from XRD, indicating no significant oxidation even after the LiOH treatment, can be confirmed. [32](#_ENREF_32)

Returning to **Figure 1a**, only the most important modes (ω1 and ω3) are discussed here, for detailed information, we refer the reader to the cited publications. Firstly, the resonant Eg mode at 123 cm-1 (ω1) corresponding to the in‑plane vibrations of the midplane titanium atoms is present for all samples and does not shift. Secondly, the ω3 mode corresponding to the A1g out‑of plane vibrations of the carbon atoms is particular sensitive to changes of the surface groups and is therefore enlarged depicted in **Figure S5b**. This ω3 mode is located at 725 cm-1 for all samples with no change upon drying for the pristine and HCl-treated samples (Ti3C2-pristine compared to Ti3C2-pristine-250C, *etc.*). However, a shift can be observed for the basic-treated samples (Ti3C2‑LiOH and Ti3C2‑LiOH‑250C) as the corresponding peak shifts to 730 cm-1, indicating a reduction of the fluorine-terminated MXene or a change in the layer thickness of the flakes.[28](#_ENREF_28)

To further investigate the change in surface groups, XPS and EDX studies were carried out, as shown in **Figure S7a** and **b**, respectively. A detailed discussion can be found in the *supporting information.* Summarizing, the aluminum content does not significantly change with other washing or drying steps and the chlorine content is also stable at ≈3 at.%. The fluorine and oxygen content also do not significantly change until the basic treatment (Ti3C2-HCl-250 compared to Ti3C2-LiOH-250C) is applied. The basic treatment leads to an increase of the oxygen content and a decrease of the fluorine content, supporting the change in the surface structure already observed by Raman spectroscopy. Obviously, EDX is not a suitable method for validating elemental changes for light elements, such as C, F and O, therefore, XPS analysis was further applied to further confirm the results.

The Ti2p core spectra shown in **Figure 2** were fitted with the restrictions and suggestions made by *Halim* *et al*. [33](#_ENREF_33) However, only the Ti, Ti2+, Ti3+ and the TiO2 component could be fitted, which is probably the result of the different synthesis method of the MAX and MXene phases. Nevertheless, it can be clearly seen that the TiO2 content increased for Ti3C2‑HCl from 4.2% to 6.1% for Ti3C2‑LiOH (**Table S2** and **Figure S11c and S12c**). Therefore, the oxidation and the removal of fluorine are indistinguishable.

****

Figure 2. Titanium core spectra fitted with restrictions made by *Halim et al*.[33](#_ENREF_33) for (a) Ti3C2‑pristine‑250C, (b) Ti3C2‑HCl-250C and (c) Ti3C2‑LiOH-250C. The calculated compositions are also listed.

Furthermore, calculating the composition of the MXene from the core spectra, the Ti to C ratio is clearly close to the theoretical value of 3/2 for all investigated samples, as depicted in **Figure 2** (complete core spectra: **Figure S8** to **S10**). In **Figure 2** also the composition of the surface groups can be seen, which shows an increase in hydroxyl groups with the basic post-treatment. However, especially the corresponding C‑Ti‑O and C‑Ti‑OH components are not distinguishable from organic components and further XPS analysis *via* sputtering would be needed. Unfortunately, sputtering does not make sense on few-layered MXenes for quantitative purposes. In addition, no Al was observable in the core spectra, further confirming the successful etching procedure, as depicted in **Figure S8f**, **S9f** and **S10f**.

Additionally, the morphology of the flakes for different MXenes is shown in **Figure S11**. The MXene particle morphology does not change upon basic or acidic post-treatment and is dominated by the agglomeration of the few layered MXenes to macroscopic flakes. Furthermore, the BET specific surface area decreases from 30.1 m2 g-1 (Ti3C2‑HCl‑250C) to 20.1 m2 g-1 (Ti3C2‑HCl‑250C) upon the basic post‑treatment (**Figure S13**).

In this first part, we wanted to answer the question if there are significant structural or chemical composition changes induced by the post-treatment of few-layered MXenes. In summary, there is no remarkable change in the surface group chemistry upon the acidic treatment of the MXene, however, a significant structural change with regard to the presence of Li cations (Ti3C2‑pristine-250C and Ti3C2-LiOH-250C). Additionally, the reduced F content, indicated by Raman spectroscopy, EDX and XPS analyses, cannot be fully separated from mild oxidation of the Ti species and, therefore, no clear suggestion can be made as also carbon impurities can be responsible for the reduced F content. Further, the shift observed in the Raman spectra can also be induced by reducing the flake size, as discussed before.

The as-synthesized MXenes (Ti3C2‑pristine‑250C, Ti3C2‑HCl‑250C, Ti3C2‑HCl‑250C; **Table S1**) were investigated by galvanostatic (rate and long-term cycling performance) and potentiostatic means to elucidate the pseudocapacitive behavior typically observed for MXenes.[1](#_ENREF_1) To get further fundamental insights into the storage mechanism, *in-situ* XRD experiments of were carried out. **Figure 3** depicts the charge/discharge rate performance of the few-layered Ti3C2*Tx* MXenes at specific currents from 0.1 A g‑1 to 5 A g‑1, which were applied with regard to the active material weight. For comparison, the C-rate was based on theoretical capacity of 320 mAh g-1 for not terminated MXene, *i.e.*, Ti3C2. [34](#_ENREF_34) Generally, the few-layered MXenes display good rate performance, *i.e.*, with a capacity of 174 mAh g-1 at 5 A g-1 (≈15.6C) for Ti3C2-HCl-250C. Especially the removal of cationic impurities and residual LiF through the acidic washing step leads to an overall improvement of the capacity regarding higher specific currents.

****

**Figure 3.** Specific de-lithiation capacity of Ti3C2*Tx* materials (Ti3C2-pristine-250C, Ti3C2-HCl-250C and Ti3C2‑LiOH-250C) in Ti3C2*Tx* || Li metal cells (half-cell setup, three-electrode configuration; potential range: 0.01 and 3 V *vs.* Li|Li+) for different specific currents.

Nevertheless, even the not post-treated Ti3C2-pristine-250C material displays a de-lithiation capacity of 155 mAh g-1 (at 5 A g-1), which is one of the highest reported in the literature so far.[1](#_ENREF_1), [11-12](#_ENREF_11), [15](#_ENREF_15) Interestingly, the de-lithiation capacity decreases for Ti3C2‑LiOH-250C for all specific currents investigated in this work (*e.g.*, 131 mAh g-1 at 5 A g-1). Moreover, after the rate performance investigation the electrodes are lithiated and de‑lithiated at 0.5 A g-1 and display high capacities of 197 mAh g-1 for Ti3C2‑pristine-250C, 237 mA g-1 for Ti3C2‑HCl-250C and 179 mAh g-1 for Ti3C2‑LiOH-250C. These capacities are even stable over 1000 charge/discharge cycles as depicted in **Figure 4**, showing the long-term cycling stability of the three different Ti3C2*Tx* materials for different specific currents ranging from 0.5 A g-1 (**Figure 4a**) to 5 A g-1 (**Figure 4c**). Besides the specific de-lithiation capacity, also the Coulombic efficiency (*C*Eff) is illustrated. A summary of the electrochemical data can be found in **Table S3** and **S4** (*supporting information*). Firstly, the different samples display capacities of 320 mAh g-1 for Ti3C2‑pristine-250C, 332 mAh g-1 for Ti3C2‑HCl-250C and 387 mAh g-1 for Ti3C2‑LiOH-250C after 1000 cycles. Moreover, a clear trend can be observed as the capacity for each sample increases from the 200th cycle compared to 1000th cycle. This behavior was also observed for delaminated MXenes (Ti3C2*Tx*) in form of free-standing electrodes and was ascribed to the electrochemical activation of the MXenes. [35-36](#_ENREF_35)



**Figure 4.**Specific de-lithiation capacity of Ti3C2*Tx* materials (Ti3C2-pristine-250C, Ti3C2-HCl-250C and Ti3C2‑LiOH-250C) in Ti3C2*Tx* || Li metal cells (half-cell setup, three-electrode configuration; potential range: 0.01 and 3 V *vs.* Li|Li+) for different specific currents during charge/discharge cycling for 1000 cycles: (a) 0.5 A g-1; (b) 1 A g-1; (c) 5 A g-1. All cells were cycled at 0.1 A g-1 for three formation cycles.

Additionally, on the one hand, Ti3C2‑pristine-250C and Ti3C2‑HCl-250C exhibit capacities at higher cycle numbers for lower charge/discharge current (0.5 A g-1), indicating a similarity in structure and composition between both materials. On the other hand, Ti3C2‑pristine-250C exhibits a local maximum after ≈50 cycles (**Figure 4a**). This effect could be due chemical reactions with impurities or due to an activation of the active material. Interestingly, Ti3C2‑LiOH-250C displays a higher capacity after 1000 cycles as Ti3C2‑pristine-250C or Ti3C2‑HCl-250C, which contrasts with the earlier described behavior during the rate performance investigation (**Figure 3**). The same behavior can also be observed for higher charge/discharge currents, *i.e.*, for 5 A g-1 (**Figure 4c**). Here, the capacities are stable after reaching a local maximum, displaying values of 116 mAh g-1 for Ti3C2‑pristine-250C, 144 mAh g-1 for Ti3C2‑HCl-250C and 176 mAh g-1 for Ti3C2‑LiOH-250C at the 1000th cycle. These differences might be due to the co‑intercalation of solvent molecules which will be analyzed and discussed below.

A first indication of this behavior can be drawn from the differential capacity profiles (d*Q*/d*V*) shown in **Figures S14-S16** for Ti3C2-pristine-250C, Ti3C2-HCl-250C and Ti3C2-LiOH-250C, respectively. Firstly, the specific de-lithiation capacity increase can be well observed in the d*Q*/d*V* profiles over the full electrode potential range. Therefore, we contribute the increase in capacity to a capacitive behavior. Further investigations are necessary, since all investigated samples (**Figure S14a, 14a and 16a**) display a significant increase of capacity from 2.5 to 3 V *vs*. Li|Li+ from the 100th to the 1000th cycle. This phenomenon could be due to the oxidation of copper, although the potential range is lower than reported values in the literature (≥3.5 V vs. Li|Li+). However, impurities do play an important role in the oxidation behavior of the current collector and can lower the oxidation potential. [37-39](#_ENREF_37)

Secondly, returning to the to the later discussed hypothesis of the co-intercalation of solvent molecules, all Ti3C2*Tx* materials exhibit two distinctive diffusion‑limited reactions at ≈1 V *vs*. Li|Li+ and ≈1.5 V *vs*. Li|Li+, during de‑lithiation (**FigureS14-S16a, c, e**). This is especially observable for higher rates and for Ti3C2‑LiOH‑250C, depicted in **Figure S16f**. Here, also the possible co-intercalation becomes visible as no distinctive, corresponding diffusion‑limited cathodic reaction can be observed, which would be expected for pseudocapacitive materials. This hysteresis behavior might be explained by the co-intercalation of the organic carbonate solvent molecules, as the intercalated molecules could hinder de‑intercalation of Li+ and, therefore, a more diffusion-limited process would be visible.

Furthermore, the acidic or basic post‑treatment of the titanium-based MXene (Ti3C2‑HCl‑250C and Ti3C2‑LiOH‑250C) influences the proposed co-intercalation of solvent molecules. Ti3C2‑HCl‑250C does not display two distinctive diffusion-limited processes at higher rates as Ti3C2‑LiOH‑250C (**Figure S15f** and **Figure S16f**), but a rather capacitive-like behavior as expected for pseudocapacitive materials. The hysteresis observed in **Figure S16f** is therefore derived from over-potentials occurring due to the high specific current. Therefore, we postulate that the acidic-treatment of MXenes hinders the co-intercalation of solvent molecules and the basic-treatment of MXenes allows for a co-intercalation of solvent molecules for the investigated electrolyte.

**Figure 5** depicts the first three cycles of cyclic voltammetry for (a) Ti3C2‑pristine-250C, (b) Ti3C2‑HCl-250C and (c) Ti3C2‑LiOH-250C, using a scan rate of 0.2 mV s-1. All samples display cathodic peaks at ≈0.7 V and ≈0.3 V *vs.* Li|Li+ in the 1st cycle, which can be correlated to the reduction of the linear and cyclic carbonates present in the electrolyte and corresponding formation of the solid electrolyte interphase (SEI).[40](#_ENREF_40) In the two subsequent cycles, two maxima are present at ≈0.8 V and ≈0.01 V *vs.* Li|Li+. The cathodic peak at ≈0.8 V *vs.* Li|Li+ can be assigned to the lithiation of the MXene as well as the peak at 0.01 V *vs.* Li|Li+, which will also contain capacity contributions from the conducting agent (=amorphous carbon). In summary, the cathodic peaks display capacitive characteristics as no clear diffusion-limited processes can be observed. [41-44](#_ENREF_41) In contrast to this, the anodic peaks display more distinguishable maxima characteristics with anodic peaks located at 0.07 V, 0.90 V, 2.25 V and an additional maximum for Ti3C2*-*LiOH-250C at 2.5 V *vs.* Li|Li+(see also **Figure S17**). Although the different MXenes display similar electrochemical characteristics, the striking difference between the samples is an anodic peak located at 0.07 V *vs*. Li|Li+, as it is only hinted for Ti3C2‑LiOH-250C (**Figure 5c**), clearly evident and decreasing with increasing cycles for Ti3C2‑HCl-250C (**Figure 5b**) and increasing and stabilizing for Ti3C2‑pristine-250C (**Figure 5a**). The origin for this current peak will be further analyzed *via* *in-situ* XRD.

For a closer look at the kinetics of the electrode reactions, different scan rates were applied. To quantify the pseudocapacitive behavior of the different Ti3C2*Tx* materials, the current should obey the power law-expression and the exponent was determined by fitting the cathodic and anodic current peaks at ≈0.8 V *vs.* Li|Li+ and ≈0.9 V *vs.* Li|Li+, respectively. The power law can be described by equation (1), where *ip* represents the measured maximum peak current, *v* the applied scan rate, and *a* and *b* represent fitting parameters.

*ip=avb (1)*

The value of *b* can be used to distinguish between diffusion-controlled and non-diffusion-controlled contributions, *i.e.*, *b=1* would be considered a pure capacitive process and *b=0.5* as purely faradaic process.[45](#_ENREF_45) The obtained values are displayed in **Figure 6a** and show a mixture of both processes. Since the few-layered Ti3C2*Tx* materials require an activation, as seen by the capacity increase over cycling, these results of course might change upon prolonged cycling.

Nevertheless, to further study the non-activated Ti3C2*Tx* materials, the non-diffusion limited capacities were calculated for all samples by using the method firstly introduced by *Ardizzone* *et al.*[46](#_ENREF_46) Here, the capacitive contribution to the overall capacity can be calculated by the fact that the capacitive contribution is not effected by the scan rate and, therefore, defined by equation (2), where *C* is the overall capacity, *C*cap represents the capacitive contribution, *v* is the scan rate and *k* is the diffusion-controlled capacity.

*C = Ccap + kv-1/2 (2)*

****

**Figure 5.** Cyclic voltammetry curves for (a) Ti3C2-pristine-250C, (b) Ti3C2-HCl-250C and (c) Ti3C2-LiOH-250C at a scan rate of 0.2 mV s-1 in a potential range from 0.01 to 3 V *vs.* Li|Li+ (half-cell setup, three-electrode configuration). The distinctive anodic and cathodic peaks are labeled accordingly.

The fitted results are depicted in **Figure 6b**, showing that *Ccap* is ≈144 mAh g-1 for Ti3C2‑pristine-250C, 202 mAh g-1 for Ti3C2‑HCl-250C and 104 mAh g-1 for Ti3C2‑LiOH-250C. This fitting allows the calculation of the non-diffusion limited capacity contribution at distinctive scan rates, as shown in **Figure S18**. Here, the Ti3C2-HCl-250C shows the lowest non-diffusion capacity contribution, as the activation of the material is not as substantial as for Ti3C2‑pristine-250C and Ti3C2‑LiOH-250C. As previously discussed, there is an increase in the overall specific de-lithiation capacity after the acidic (HCl) washing step, while the capacity decreases again after the basic (LiOH) treatment.

****

**Figure 6.** (a) Calculated b parameters for Ti3C2-pristine-250C, Ti3C2-HCl-250C and Ti3C2-LiOH-250C. (b) Calculated Ccap for the later mentioned MXenes by linear fitting against v-1/2. (half-cell setup, three-electrode configuration; potential range: 0.01 and 3 V *vs.* Li|Li+).

To gain fundamental understanding of the lithiation/de-lithiation behavior of the MXenes, *in-situ* XRD investigations for the Ti3C2-pristine-250C (**Figure 7**), Ti3C2-HCl-250C (**Figure 8**) and Ti3C2-LiOH-250C (**Figure 9**) samples were conducted for three charge/discharge cycles. The *in-situ* XRD cell was galvanostatically cycled and the results were fitted with a pseudo‑Voigt function. In the 1st cycle, only the distinctive points marked in the voltage-time plot (right graphs in **Figures 7, 8** and **9**) were fitted for all samples. The fitted reflections can be found in the supporting information (**Figures S19, S20** and **S21**). Furthermore, only the (002) reflection was fitted as it displays the highest intensity. Nevertheless, (002) and (004) reflections are both shown in **Figures 7, 8** and **9**. To the best of our knowledge, MXenes have been investigated *via* *in-situ* XRD only for the use as a negative electrode material in supercapacitors so far. *Lin* *et al.* and *Wang* *et al.* have both studied free-standing, single-layered Ti3C2*Tx* MXenes in ionic liquids as well as sulfoxide-, carbonate- and nitrile-based electrolytes. [47-48](#_ENREF_47) From their works important electrochemical characteristics could be derived, which significantly improved the understanding of MXenes. However, LIB negative electrodes are usually operated at much lower potentials and, furthermore, only MXene flakes were investigated so far. Therefore, we conducted *in-situ* XRD experiments for few-layered Ti3C2*Tx* to decipher the above presented electrochemical results regarding the acidic and basic treatment.

Generally, comparing the results of all three samples, the similarity between Ti3C2‑pristine‑250C and Ti3C2‑LiOH‑250C is obvious (**Figure 7** and **Figure 9**). Qualitatively, the intensity of the (002) reflection increases in intensity with lithiation and decreases upon de-lithiation. Additionally, a shift of the reflection towards lower 2θ values can be observed. The opposite of this behavior is present for Ti3C2‑HCl‑250C (**Figure 8**), as no shift can be observed, and the intensity of the reflection diminished upon lithiation. Due to the similarity of the Ti3C2‑pristine‑250C and Ti3C2‑LiOH‑250C samples and for reasons of simplicity, only LiOH is discussed here, while the discussion on Ti3C2-pristine-250C can be found in the *supporting information* (**Figure S19**). Firstly, no difference between the Ti3C2-HCl-250C material (powder) and the composite electrode can be detected as both samples display a reflection at 8.3° and 17° 2θ, which correspond to the shifted (002) and (004) reflections of Ti3AlC2, as discussed above (**Figure S20a,** ‘1/start’and **Figure** **S1**). Therefore, intercalation of solvent molecules does not occur spontaneously for Ti3C2-HCl-250C. Upon lithiation, a reflection emerges at ≈9.3° 2θ (**Figure S20a**,’1/I’, 0.95 V) which continuously increases in relative area size (**Figure S20b** and **c**, ‘1/II’, 0.44 V), which will be referred to as ‘HCl-Reflex 2’. Despite the emerging reflection, the first reflection (‘HCl-Reflex 1’) remains constant at 8.3° 2θ. Further lithiation leads to a shift of ‘HCl-Reflex 1’ to 8.0° 2θ (‘1/III’, 0.25 V) and 7.74° 2θ after the full lithiation is reached (‘1/IV’, 0.01 V), as depicted in **Figure S20d** and **e**. Upon de-lithiation, the ‘HCl-Reflex 1’ shifts back to higher 2θ values (**Figure S20f** and **g**, ‘1/V’ and ‘1/VI’, 0.83 V and 2.5 V) and remains at 7.9° at the end of discharge (**Figure S20g**, ‘1/End’, 3 V). The relative area and intensity increase for ‘HCl-Reflex 1’ and the FWHM decreases upon de‑lithiation. This indicates a more ordered structure in the de‑lithiated state for ‘HCl‑Reflex 1’ (**Figure S20g** and **h**). Nevertheless, ‘HCl‑Reflex 2’ remains at 8.8° 2θ, suggesting trapped Li+ ions between the sheets, resulting in a decreased interspace layer (**Figure S20h**).

****

**Figure 7**. *Left:* Heat map for the *in-situ* XRD analysis of Ti3C2-pristine-250C for the first three cycles showing the (002) and (004) reflections ranging from high intensity (red) to low intensity (purple). *Right:* The corresponding voltage response plotted against the time (cell voltage range: 0.01-3 V; specific current: 20 mA g-1). The discussed points are marked with Latin numbers for cycle (1-3) and Greek numbers for the highlighted points.

****

**Figure 8.** *Left:* Heat map for the *in-situ* XRD analysis of Ti3C2-HCl-250C for the first three cycles showing the (002) and (004) reflections ranging from high intensity (red) to low intensity (purple). *Right:* The corresponding voltage response plotted against the time (cell voltage range: 0.01-3 V; specific current: 20 mA g-1). The discussed points are marked with Latin numbers for cycle (1-3) and Greek numbers for the highlighted points.

The behavior of HCl‑‘HCl-Reflex 1’ can be explained by the electrostatic repulsion occurring between the MXene layers, which upon lithiation leads to a shrinkage of the interlayer space as the Li+ ions attract the layers. [24](#_ENREF_24), [49](#_ENREF_49) Secondly, the shift of ‘HCl-Reflex 1’ can be explained by co-intercalation of solvent molecules or anionic species, as it has been shown in the literature.[47](#_ENREF_47), [50-51](#_ENREF_50) *Wang et al*. recently showed that the intercalation of solvent molecules heavily depends on the used solvent and their properties towards the solvation of the cation.[48](#_ENREF_48) As this is the first time few-layered MXenes are investigated *via in-situ* XRD for LIB cells and also two distinctive reflections are observed for Ti3C2*Tx*, we allocate the second reflection (‘HCl-HCl‑Reflex 2’) to the intercalation of Li+ ions *into* the few-layered MXenes and the shift of the first reflection (‘HCl‑Reflex 1’) to the intercalation of Li+ ions *between* agglomerated few-layered MXenes and the simultaneous co-intercalation of solvent molecules. This is supported by the lower FWHM value observed for ‘HCl‑Reflex 1’ due to solvent co-intercalation, as described before for the intercalation of water molecules (see **Figure S20b‑h**). This two‑step intercalation behavior can be responsible for the high capacity retention for high specific currents, since the intercalation of Li+ ions between the agglomerated few-layered MXenes should be kinetically favored compared to the intercalation into few‑layered Ti3C2*Tx*. Therefore, this effect can buffer the overpotentials from the bulk process, leading to an increased capacity retention at high current rates (**Figure 3**). Moreover, this assumption is supported by the fact that the activation shown in **Figure 4**, occurs faster for higher currents (5 A g-1, **Figure 4c**) than for lower currents (0.5 A g-1; **Figure 4a**). This is also supported by the high reversibility of the later described behavior shown in **Figure 8** and **Figure 10**. The fitted positions of both reflections (µ, ‘HCl‑Reflex 1’ and ‘HCl‑Reflex 2’; blue curves) and the corresponding voltage *vs*. time diagram are shown in **Figure 10a** and**10b**, respectively. Here, the same behavior as described for the first cycle can be observed for the 2nd and 3rd cycle. The constant µ for ‘HCl‑Reflex 1’ in a voltage range of ≈1 V is especially striking (**Figure 10b**), correlating with the maxima observed in the cyclic voltammetry measurements (**Figure 5**). Further, it shows that the diffusion-limited process does not correlate to any changes in the structure of Ti3C2-HCl-250Cand, therefore, supports the pseudocapacitive properties of Ti3C2*Tx*. The limitation of the diffusion can be related to the co-intercalation of solvent molecules. However, further studies are necessary to prove this hypothesis. Furthermore, at ≈2.5 V (‘2/VI’ and ‘3/VI’) there is a shift of ‘HCl‑Reflex 1’ towards higher 2θ values, indicating that a higher voltage is necessary to reach a fully de-lithiated state (**Figure 8** and **Figure 10**).

Comparing the *in-situ* XRD results of the HCl- (Ti3C2‑HCl‑250C, **Figure 8**) and the LiOH-treated samples (Ti3C2‑LiOH‑250C, **Figure 9**), the diffractograms display significant, structural differences. Firstly, at the beginning of the first lithiation (**Figure S21a**, ‘1/start’, 3 V) the (002) reflection is fitted with three reflections, named ‘LiOH-Reflex 1 to 3’, displaying 2θ values of 7.1°, 7.4° and 8.0°. This indicates a spontaneous intercalation of solvent molecules, contrary to Ti3C2-HCl-250C.

****

**Figure 9.** *Left:* Heat map for the *in-situ* XRD analysis of Ti3C2-LiOH-250C for the first three cycles showing the (002) and (004) reflections ranging from high intensity (red) to low intensity (purple). *Right:* The corresponding voltage response plotted against the time (voltage range: 0.01-3 V; specific current: 20 A g-1). The discussed points are marked with Latin numbers for cycle (1-3) and Greek numbers for the highlighted points.

Upon the first lithiation, a general shift is visible for the (002) reflection towards lower 2θ values (**Figure 9**, ‘1/I’ to ‘1/II’, 0.87 V to 0.48 V) and the intensity decreases to a cell voltage of 0.29 V (**Figure 9**, ‘1/III’), which agrees with the *in-situ* XRD results for Ti3C2‑HCl‑250C. However, the deconvolution of the (002) reflection shows the significant difference between the basic and the acidic post-treatment of Ti3C2*Tx* (**Figure S21b-d**). As the lithiation progresses, the three reflections (‘LiOH-Reflex 1‑3’, **Figure S21b-c**, ‘1/I’ and ‘1/II’, 0.87 and 0.48 V) only change in *area1‑3*, but their position *µ1‑3*does not change significantly, while *area1-2* increases in relation to *area3*. Moreover, ‘LiOH-Reflex 2’ and ‘LiOH-Reflex 3’ merge into one reflection and ‘LiOH‑Reflex 1’ almost vanishes (**Figure S21d**, ‘1/IV’, 0.21 V). Further lithiation of Ti3C2‑LiOH‑250C leads to a sudden increase of the intensity of the overall (002) reflection and to a shift towards lower 2θ values (**Figure 9**, ‘1/IV’ to ‘1/V’, 0.21 V to 0.01 V). This structural change during lithiation is in strong contrast to the behavior observed for Ti3C2‑HCl‑250C.

In **Figure S21**, it is evident that only the ‘Reflex‑LiOH 3’ is present and ‘LiOH‑Reflex 1’ has vanished. At the end of lithiation, ‘LiOH‑Reflex 3’ shifts from 7.2° to 6.9° 2θ and the FWHM decreases from 0.8° to 0.6°, indicating that the degree of crystallinity increases with the degree of lithiation (**Figure S21e-f**, ‘1/IV’ to ‘1/V’, 0.21 to 0.01 V). Upon de-lithiation, the interspace layer and the intensity decrease again (**Figure 10, ‘**1/VI’, 0.96 V). Further de‑lithiation leads to an increase of 2θ, from 7.1° (‘1/VI’, 0.96 V) to 7.2° (‘1/VII’, 2.5V) and to 7.3° (‘1/End’, 3 V), as depicted in **Figure S21g-i**. Interestingly, the FWHM also increases again from 1.3° to 1.1° (‘1/VII’ to ‘1/End’, 2.5 to 3 V). During de-lithiation and also for the subsequent cycles, there is only one reflection visible (**Figure 10a and Figure S21f-i**, ‘1/V’ to ‘1/End’, 0.01 V to 3V). Firstly, we allocate the three reflections (**Figure S21a-c**, ‘I/start’-‘1/II’, 3‑0.48 V) to at least two different stages of co-intercalation occurring during the lithiation. Here, ‘LiOH-Reflex 1’ and LiOH-Reflex 2’ represent two different stages of the intercalation of solvated Li+ ions *between* the few-layered sheets, while ‘LiOH-Reflex 1’ refers to the intercalation *into* the few-layered Ti3C2*Tx*. This is supported by the fact, that with further lithiation all deconvoluted reflections merge into a single reflection at a potential of 0.21 V (**Figure S21**, ‘I/IV’). Furthermore, since only a single reflection and no second reflection at a higher 2θ values is visible, like for Ti3C2‑HCl‑250C, the electrostatic attraction between Li+ and the negatively charged surface of the MXene is lifted due to co-intercalation of the solvent. Therefore, no structural difference exists after the first lithiation between the intercalation *between* and *into* the few-layered MXenes, in contrast to the acidic treated sample (Ti3C2-HCl-250C). Furthermore this observation leads to the conclusion that the solvation shell does desolvate for few-layered Ti3C2*Tx*, as it has been observed for Ti2C*Tx* by *ex-situ* XRD results.[49](#_ENREF_49) The solvent co-intercalation is also responsible for the reduced capacity (**Figure 3**), similar to the results shown by *Wang* *et al*. for supercapacitors.[48](#_ENREF_48) This hypothesis can also explain the activation of the MXene by an effective SEI layer, hindering the co-intercalation of solvent molecules and, therefore, resulting in an increase of specific capacity.

****

**Figure 10.** Results of the pseudo-Voigt fitting of the (002) reflection of the *in-situ* XRD analysis with two reflections showing in (a) the mean 2θ value (µ) of each reflection and (b) the corresponding voltage response plotted against the time. The discussed points are marked with Latin numbers for the 2nd and 3rd cycle and Greek numbers for the highlighted points.

Since no significant changes to the surface groups were detected and the only difference between Ti3C2-HCl-250C and Ti3C2-LiOH-250C is the intercalation of Li+ ions during the basic post-treatment, this behavior could be triggered by the pre‑intercalation of Li+ ions. However, further systematic *in-situ* XRD investigations are necessary to confirm this hypothesis.

**Conclusion**

In this work, a synthesis and post-treatment route was established to etch and synthesize few-layered Ti3C2*Tx*‑based MXenes from the respective MAX phases for application as negative electrode in lithium ion battery (LIB) cells. Firstly, the as‑synthesized materials and changes induced *via* an acidic (HCl) and basic (LiOH) post‑treatment were systematically characterized *via* XRD, Raman spectroscopy, XPS and EDX to decipher structural changes with an emphasis on the change of the surface groups of Ti3C2*Tx*. We aimed to answer three scientific questions to achieve an improved fundamental understanding on the implications of acidic or basic post-treatment.

Firstly, we wanted to clarify if the post-treatment induces any significant structural or chemical compositional changes for few-layered MXenes. Besides a small oxidation and a decrease in the fluorine content of Ti3C2*Tx* occurring during the LiOH-post-treatment, no significant chemical changes were detected. Furthermore, the XRD investigations under ambient and Ar atmosphere revealed the literature‑known intercalation of water molecules, if Li+ ions are present in the MXene structure, which are intercalated during synthesis. Moreover, no significant morphological changes were detected for the few-layered MXene upon any post-treatment. In summary, the only significant change occurring after the acidic- and basic-treatment is the removal or placement of alkali cations, which influence the MXene behavior towards water molecules in ambient air.

Secondly, we aimed to elucidate if changes induced by the post-treatment correlate to a change in the electrochemical performance, especially regarding the diffusion- and non-diffusion-limited processes. Therefore, the electrochemical impact of the basic or acidic post-treatment was investigated by galvanostatic and potentiostatic means. The few-layered MXenes fortified their potential as a high-power negative electrode material with a stable capacity retention of over 1000 cycles due to their pseudocapacitive behavior. The acidic post-treatment of Ti3C2*Tx* lowered the non-diffusion-limited capacity in comparison to the basic post-treatment, which led to an increase in the overall specific de-lithiation capacity.

Thirdly, we intended to elaborate if the changes in electrochemical performance are induced by structural changes of the active material. Thereby, the increase in the specific capacity of the acidic-treated Ti3C2*Tx* could be assigned to a reduced solvent co-intercalation as shown by the deconvolution of the (002) reflection recorded *via* *in-situ* XRD. In contrast, the basic-treated MXene underwent huge structural changes during the (de)lithiation in the initial charge/discharge cycles, which was attributed to the co-intercalation of the cyclic or linear carbonates from the electrolyte (**Figure 11**).

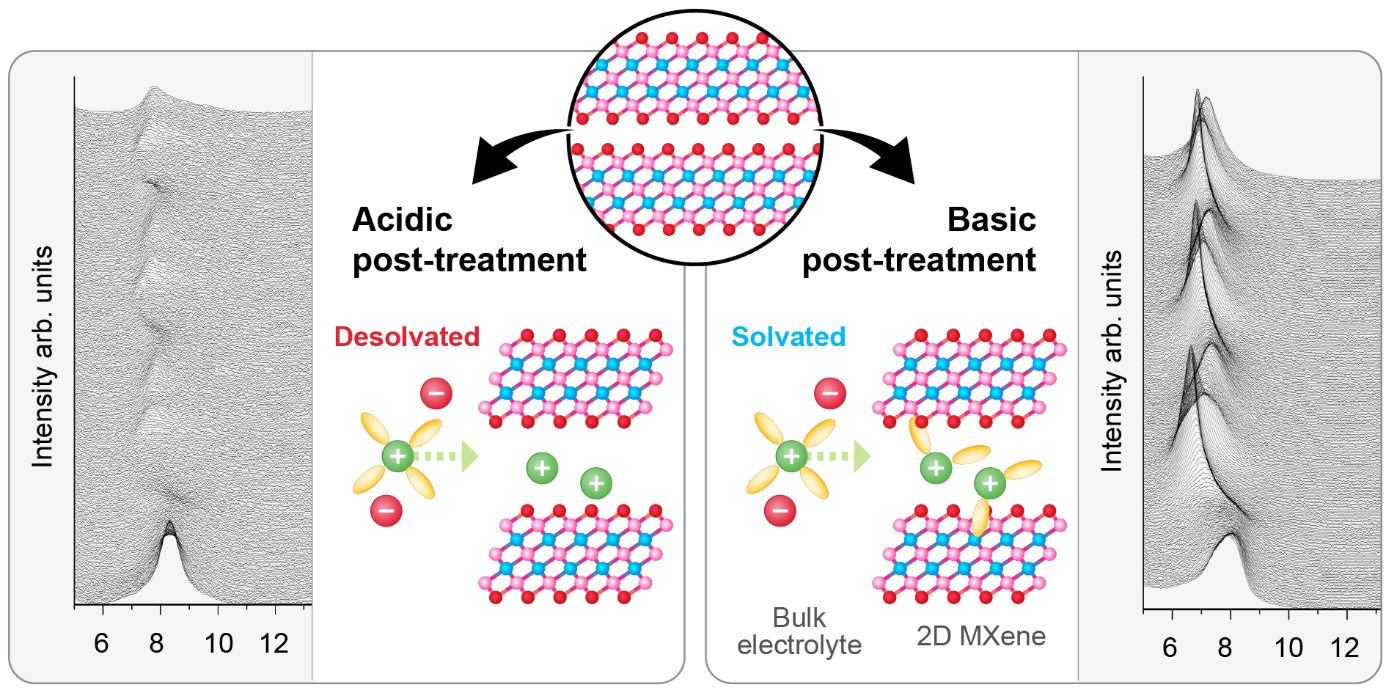
****

Figure 11. Schematic conclusion on the role of the acidic and basic post-treatment of Ti3C2T*x* MXenes on the electrochemical behavior as negative electrode in LIB cells, pointing out the solvent co-intercalation for the basic-treated samples, as detected by *in-situ* XRD studies.

All in all, the presence/absence of lithium cations in the MXene host structure, induced by the basic(pristine)/acidic‑treatment, significantly decreases/increases the non-diffusion limited processes, which can be directly correlated to the occurring/inhibited co-intercalation of solvent molecules from the electrolyte. Overall, this study clearly underlines the importance of further systematic studies on the co-intercalationa of solvent molecules during (de)lithiation, especially focusing on the long-term stability and solid electrolyte interphase formation during the initial cycles.

**Supporting Information**

Overview of samples and abbreviations, synthesis details for Ti3AlC2 MAX phases and Ti3C2T*x* MXenes, details of electrode preparation and analytical and electrochemical characterization methods, XRD patterns, thermogravimetric analysis, Raman spectra, XPS and EDX survey spectra, XPS core spectra, Table on Binding energies, FWHM, areas and concentrations (from XPS analysis), SEM images and EDX elemental mappings, nitrogen adsorption/ desorption curves, Tables and Figures summarizing electrochemical data, d*Q*/d*V* profiles, Figures on fitted reflections from *in-situ* XRD analyses.

**Notes**

The authors declare no competing financial interest.

**Acknowledgements**

The authors thank the Ministry of Economic Affairs, Innovation, Digitalization and Energy of the State of North Rhine-Westphalia (MWIDE) for funding this work in the project ‘GrEEn’ (313-W044A). We also thank Andre Bar for graphical support.

**References**

(1) Anasori, B.; Lukatskaya, M. R.; Gogotsi, Y. 2D metal carbides and nitrides (MXenes) for energy storage. *Nat. Rev. Mater.* **2017,** *2* (2), 16098, DOI: 10.1038/natrevmats.2016.98.

(2) Naguib, M.; Kurtoglu, M.; Presser, V.; Lu, J.; Niu, J.; Heon, M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-Dimensional Nanocrystals Produced by Exfoliation of Ti3AlC2. *Adv. Mater.* **2011,** *23* (37), 4248-4253, DOI: 10.1002/adma.201102306.

(3) Pang, J.; Mendes, R. G.; Bachmatiuk, A.; Zhao, L.; Ta, H. Q.; Gemming, T.; Liu, H.; Liu, Z.; Rummeli, M. H. Applications of 2D MXenes in energy conversion and storage systems. *Chem. Soc. Rev.* **2019,** *48* (1), 72-133, DOI: 10.1039/C8CS00324F.

(4) Chen, X.; Zhu, Y.; Zhang, M.; Sui, J.; Peng, W.; Li, Y.; Zhang, G.; Zhang, F.; Fan, X. N-Butyllithium-Treated Ti3C2Tx MXene with Excellent Pseudocapacitor Performance. *ACS Nano* **2019,** *13* (8), 9449-9456, DOI: 10.1021/acsnano.9b04301.

(5) Dong, Y.; Wu, Z.-S.; Zheng, S.; Wang, X.; Qin, J.; Wang, S.; Shi, X.; Bao, X. Ti3C2 MXene-Derived Sodium/Potassium Titanate Nanoribbons for High-Performance Sodium/Potassium Ion Batteries with Enhanced Capacities. *ACS Nano* **2017,** *11* (5), 4792-4800, DOI: 10.1021/acsnano.7b01165.

(6) Lian, P.; Dong, Y.; Wu, Z.-S.; Zheng, S.; Wang, X.; Sen, W.; Sun, C.; Qin, J.; Shi, X.; Bao, X. Alkalized Ti3C2 MXene nanoribbons with expanded interlayer spacing for high-capacity sodium and potassium ion batteries. *Nano Energy* **2017,** *40*, 1-8, DOI: https://doi.org/10.1016/j.nanoen.2017.08.002.

(7) Luo, J.; Tao, X.; Zhang, J.; Xia, Y.; Huang, H.; Zhang, L.; Gan, Y.; Liang, C.; Zhang, W. Sn4+ Ion Decorated Highly Conductive Ti3C2 MXene: Promising Lithium-Ion Anodes with Enhanced Volumetric Capacity and Cyclic Performance. *ACS Nano* **2016,** *10* (2), 2491-2499, DOI: 10.1021/acsnano.5b07333.

(8) Shuck, C. E.; Han, M.; Maleski, K.; Hantanasirisakul, K.; Kim, S. J.; Choi, J.; Reil, W. E. B.; Gogotsi, Y. Effect of Ti3AlC2 MAX Phase on Structure and Properties of Resultant Ti3C2Tx MXene. *ACS Appl. Nano Mater.* **2019,** *2* (6), 3368-3376, DOI: 10.1021/acsanm.9b00286.

(9) Kajiyama, S.; Szabova, L.; Sodeyama, K.; Iinuma, H.; Morita, R.; Gotoh, K.; Tateyama, Y.; Okubo, M.; Yamada, A. Sodium-Ion Intercalation Mechanism in MXene Nanosheets. *ACS Nano* **2016,** *10* (3), 3334-3341, DOI: 10.1021/acsnano.5b06958.

(10) Yan, J.; Ren, C. E.; Maleski, K.; Hatter, C. B.; Anasori, B.; Urbankowski, P.; Sarycheva, A.; Gogotsi, Y. Flexible MXene/Graphene Films for Ultrafast Supercapacitors with Outstanding Volumetric Capacitance. *Adv. Funct. Mater.* **2017,** *27* (30), 1701264, DOI: 10.1002/adfm.201701264.

(11) Chaudhari, N. K.; Jin, H.; Kim, B.; San Baek, D.; Joo, S. H.; Lee, K. MXene: an emerging two-dimensional material for future energy conversion and storage applications. *J. Mater. Chem. A* **2017,** *5* (47), 24564-24579, DOI: 10.1039/C7TA09094C.

(12) Tang, H.; Hu, Q.; Zheng, M.; Chi, Y.; Qin, X.; Pang, H.; Xu, Q. MXene–2D layered electrode materials for energy storage. *Prog. Nat. Sci.: Mater. Int.* **2018,** *28* (2), 133-147, DOI: https://doi.org/10.1016/j.pnsc.2018.03.003.

(13) Mashtalir, O.; Naguib, M.; Mochalin, V. N.; Dall’Agnese, Y.; Heon, M.; Barsoum, M. W.; Gogotsi, Y. Intercalation and delamination of layered carbides and carbonitrides. *Nat. Commun.* **2013,** *4* (1), 1716, DOI: 10.1038/ncomms2664.

(14) Xiong, D.; Li, X.; Bai, Z.; Lu, S. Recent Advances in Layered Ti3C2Tx MXene for Electrochemical Energy Storage. *Small* **2018,** *14* (17), 1703419, DOI: 10.1002/smll.201703419.

(15) Zhang, X.; Zhang, Z.; Zhou, Z. MXene-based materials for electrochemical energy storage. *J. Energy Chem.* **2018,** *27* (1), 73-85, DOI: https://doi.org/10.1016/j.jechem.2017.08.004.

(16) Natu, V.; Hart, J. L.; Sokol, M.; Chiang, H.; Taheri, M. L.; Barsoum, M. W. Edge Capping of 2D-MXene Sheets with Polyanionic Salts To Mitigate Oxidation in Aqueous Colloidal Suspensions. *Angew. Chem., Int. Ed.* **2019,** *58* (36), 12655-12660, DOI: 10.1002/anie.201906138.

(17) Natu, V.; Sokol, M.; Verger, L.; Barsoum, M. W. Effect of Edge Charges on Stability and Aggregation of Ti3C2Tz MXene Colloidal Suspensions. *J. Phys. Chem. C* **2018,** *122* (48), 27745-27753, DOI: 10.1021/acs.jpcc.8b08860.

(18) Seyedin, S.; Zhang, J.; Usman, K. A. S.; Qin, S.; Glushenkov, A. M.; Yanza, E. R. S.; Jones, R. T.; Razal, J. M. Facile Solution Processing of Stable MXene Dispersions towards Conductive Composite Fibers. *Global Challenges* **2019,** *3* (10), 1900037, DOI: 10.1002/gch2.201900037.

(19) Zhang, C. J.; Pinilla, S.; McEvoy, N.; Cullen, C. P.; Anasori, B.; Long, E.; Park, S.-H.; Seral-Ascaso, A.; Shmeliov, A.; Krishnan, D.; Morant, C.; Liu, X.; Duesberg, G. S.; Gogotsi, Y.; Nicolosi, V. Oxidation Stability of Colloidal Two-Dimensional Titanium Carbides (MXenes). *Chem. Mater.* **2017,** *29* (11), 4848-4856, DOI: 10.1021/acs.chemmater.7b00745.

(20) Célérier, S.; Hurand, S.; Garnero, C.; Morisset, S.; Benchakar, M.; Habrioux, A.; Chartier, P.; Mauchamp, V.; Findling, N.; Lanson, B.; Ferrage, E. Hydration of Ti3C2Tx MXene: An Interstratification Process with Major Implications on Physical Properties. *Chem. Mater.* **2019,** *31* (2), 454-461, DOI: 10.1021/acs.chemmater.8b03976.

(21) Ghidiu, M.; Halim, J.; Kota, S.; Bish, D.; Gogotsi, Y.; Barsoum, M. W. Ion-Exchange and Cation Solvation Reactions in Ti3C2 MXene. *Chem. Mater.* **2016,** *28* (10), 3507-3514, DOI: 10.1021/acs.chemmater.6b01275.

(22) Voigt, C. A.; Ghidiu, M.; Natu, V.; Barsoum, M. W. Anion Adsorption, Ti3C2Tz MXene Multilayers, and Their Effect on Claylike Swelling. *J. Phys. Chem. C* **2018,** *122* (40), 23172-23179, DOI: 10.1021/acs.jpcc.8b07447.

(23) Ghidiu, 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, DOI: 10.1038/nature13970.

(24) Levi, M. D.; Lukatskaya, M. R.; Sigalov, S.; Beidaghi, M.; Shpigel, N.; Daikhin, L.; Aurbach, D.; Barsoum, M. W.; Gogotsi, Y. Solving the Capacitive Paradox of 2D MXene using Electrochemical Quartz-Crystal Admittance and In Situ Electronic Conductance Measurements. *Adv. Energy Mater.* **2015,** *5* (1), 1400815, DOI: 10.1002/aenm.201400815.

(25) Lukatskaya, M. R.; Mashtalir, O.; Ren, C. E.; Dall’Agnese, Y.; Rozier, P.; Taberna, P. L.; Naguib, M.; Simon, P.; Barsoum, M. W.; Gogotsi, Y. Cation Intercalation and High Volumetric Capacitance of Two-Dimensional Titanium Carbide. *Science* **2013,** *341* (6153), 1502, DOI: 10.1126/science.1241488.

(26) Verger, L.; Natu, V.; Ghidiu, M.; Barsoum, M. W. Effect of Cationic Exchange on the Hydration and Swelling Behavior of Ti3C2Tz MXenes. *J. Phys. Chem. C* **2019,** *123* (32), 20044-20050, DOI: 10.1021/acs.jpcc.9b04546.

(27) Hu, T.; Wang, J.; Zhang, H.; Li, Z.; Hu, M.; Wang, X. Vibrational properties of Ti3C2 and Ti3C2T2 (T = O, F, OH) monosheets by first-principles calculations: a comparative study. *Phys. Chem. Chem. Phys.* **2015,** *17* (15), 9997-10003, DOI: 10.1039/C4CP05666C.

(28) Lioi, D. B.; Neher, G.; Heckler, J. E.; Back, T.; Mehmood, F.; Nepal, D.; Pachter, R.; Vaia, R.; Kennedy, W. J. Electron-Withdrawing Effect of Native Terminal Groups on the Lattice Structure of Ti3C2Tx MXenes Studied by Resonance Raman Scattering: Implications for Embedding MXenes in Electronic Composites. *ACS Appl. Nano Mater.* **2019**, DOI: 10.1021/acsanm.9b01194.

(29) Balachandran, U.; Eror, N. G. Raman spectra of titanium dioxide. *J. Solid State Chem.* **1982,** *42* (3), 276-282, DOI: https://doi.org/10.1016/0022-4596(82)90006-8.

(30) Ferrari, A. C.; Robertson, J. Interpretation of Raman spectra of disordered and amorphous carbon. *Phys. Rev. B* **2000,** *61* (20), 14095-14107, DOI: 10.1103/PhysRevB.61.14095.

(31) Sadezky, A.; Muckenhuber, H.; Grothe, H.; Niessner, R.; Pöschl, U. Raman microspectroscopy of soot and related carbonaceous materials: Spectral analysis and structural information. *Carbon* **2005,** *43* (8), 1731-1742, DOI: https://doi.org/10.1016/j.carbon.2005.02.018.

(32) Ahmed, B.; Anjum, D. H.; Hedhili, M. N.; Gogotsi, Y.; Alshareef, H. N. H2O2 assisted room temperature oxidation of Ti2C MXene for Li-ion battery anodes. *Nanoscale* **2016,** *8* (14), 7580-7587, DOI: 10.1039/C6NR00002A.

(33) Halim, J.; Cook, K. M.; Naguib, M.; Eklund, P.; Gogotsi, Y.; Rosen, J.; Barsoum, M. W. X-ray photoelectron spectroscopy of select multi-layered transition metal carbides (MXenes). *Appl. Surf. Sci.* **2016,** *362*, 406-417, DOI: https://doi.org/10.1016/j.apsusc.2015.11.089.

(34) Xie, Y.; Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y.; Yu, X.; Nam, K.-W.; Yang, X.-Q.; Kolesnikov, A. I.; Kent, P. R. C. Role of Surface Structure on Li-Ion Energy Storage Capacity of Two-Dimensional Transition-Metal Carbides. *J. Am. Chem. Soc.* **2014,** *136* (17), 6385-6394, DOI: 10.1021/ja501520b.

(35) Ren, C. E.; Zhao, M.-Q.; Makaryan, T.; Halim, J.; Boota, M.; Kota, S.; Anasori, B.; Barsoum, M. W.; Gogotsi, Y. Porous Two-Dimensional Transition Metal Carbide (MXene) Flakes for High-Performance Li-Ion Storage. *ChemElectroChem* **2016,** *3* (5), 689-693, DOI: 10.1002/celc.201600059.

(36) Zeng, G.; Shi, N.; Hess, M.; Chen, X.; Cheng, W.; Fan, T.; Niederberger, M. A General Method of Fabricating Flexible Spinel-Type Oxide/Reduced Graphene Oxide Nanocomposite Aerogels as Advanced Anodes for Lithium-Ion Batteries. *ACS Nano* **2015,** *9* (4), 4227-4235, DOI: 10.1021/acsnano.5b00576.

(37) Aurbach, D. Morphological Studies of Li Deposition Processes in LiAsF[sub 6]∕PC Solutions by In Situ Atomic Force Microscopy. *J. Electrochem. Soc.* **1997,** *144* (10), 3355, DOI: 10.1149/1.1838018.

(38) Myung, S.-T.; Hitoshi, Y.; Sun, Y.-K. Electrochemical behavior and passivation of current collectors in lithium-ion batteries. *J. Mater. Chem.* **2011,** *21* (27), 9891-9911, DOI: 10.1039/C0JM04353B.

(39) Zhao, M.; Kariuki, S.; Dewald, H.; Lemke, F.; Staniewicz, R.; Plichta, E.; Marsh, R. Electrochemical Stability of Copper in Lithium‐Ion Battery Electrolytes. *J. Electrochem. Soc.* **2000,** *147*, 2874-2879, DOI: 10.1149/1.1393619.

(40) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **2004,** *104* (10), 4303-4418, DOI: 10.1021/cr030203g.

(41) Cheng, R.; Hu, T.; Zhang, H.; Wang, C.; Hu, M.; Yang, J.; Cui, C.; Guang, T.; Li, C.; Shi, C.; Hou, P.; Wang, X. Understanding the Lithium Storage Mechanism of Ti3C2Tx MXene. *J. Phys. Chem. C* **2019,** *123* (2), 1099-1109, DOI: 10.1021/acs.jpcc.8b10790.

(42) Augustyn, V.; Simon, P.; Dunn, B. Pseudocapacitive oxide materials for high-rate electrochemical energy storage. *Energy Environ. Sci.* **2014,** *7* (5), 1597-1614, DOI: 10.1039/C3EE44164D.

(43) Conway, B. E. Transition from “Supercapacitor” to “Battery” Behavior in Electrochemical Energy Storage. *J. Electrochem. Soc.* **1991,** *138* (6), 1539-1548.

(44) Simon, P.; Gogotsi, Y.; Dunn, B. Where Do Batteries End and Supercapacitors Begin? *Science* **2014,** *343* (6176), 1210, DOI: 10.1126/science.1249625.

(45) Lindström, H.; Södergren, S.; Solbrand, A.; Rensmo, H.; Hjelm, J.; Hagfeldt, A.; Lindquist, S.-E. Li+ Ion Insertion in TiO2 (Anatase). 2. Voltammetry on Nanoporous Films. *J. Phys. Chem. B* **1997,** *101* (39), 7717-7722, DOI: 10.1021/jp970490q.

(46) Ardizzone, S.; Fregonara, G.; Trasatti, S. “Inner” and “outer” active surface of RuO2 electrodes. *Electrochim. Acta* **1990,** *35* (1), 263-267, DOI: https://doi.org/10.1016/0013-4686(90)85068-X.

(47) Lin, Z.; Barbara, D.; Taberna, P.-L.; Van Aken, K. L.; Anasori, B.; Gogotsi, Y.; Simon, P. Capacitance of Ti3C2Tx MXene in ionic liquid electrolyte. *J. Power Sources* **2016,** *326*, 575-579, DOI: https://doi.org/10.1016/j.jpowsour.2016.04.035.

(48) Wang, X.; Mathis, T. S.; Li, K.; Lin, Z.; Vlcek, L.; Torita, T.; Osti, N. C.; Hatter, C.; Urbankowski, P.; Sarycheva, A.; Tyagi, M.; Mamontov, E.; Simon, P.; Gogotsi, Y. Influences from solvents on charge storage in titanium carbide MXenes. *Nat. Energy* **2019,** *4* (3), 241-248, DOI: 10.1038/s41560-019-0339-9.

(49) Okubo, M.; Sugahara, A.; Kajiyama, S.; Yamada, A. MXene as a Charge Storage Host. *Acc. Chem. Res.* **2018,** *51* (3), 591-599, DOI: 10.1021/acs.accounts.7b00481.

(50) Dall’Agnese, Y.; Rozier, P.; Taberna, P.-L.; Gogotsi, Y.; Simon, P. Capacitance of two-dimensional titanium carbide (MXene) and MXene/carbon nanotube composites in organic electrolytes. *J. Power Sources* **2016,** *306*, 510-515, DOI: https://doi.org/10.1016/j.jpowsour.2015.12.036.

(51) Kajiyama, S.; Szabova, L.; Iinuma, H.; Sugahara, A.; Gotoh, K.; Sodeyama, K.; Tateyama, Y.; Okubo, M.; Yamada, A. Enhanced Li-Ion Accessibility in MXene Titanium Carbide by Steric Chloride Termination. *Adv. Energy Mater.* **2017,** *7* (9), 1601873, DOI: 10.1002/aenm.201601873.