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Effect of Cationic Exchange on the Hydration and Swelling Behavior of $\text{Ti}_3\text{C}_2\text{T}_z$ MXenes

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Abstract

MXenes, two dimensional (2D) transition metal carbides, have showed great promise as materials for capacitive energy storage, electromagnetic interference shielding, transparent electrodes, among many other applications. Colloidal suspensions are usually processed to design materials for these applications. However, the mechanisms underlying the MXene exfoliation into single or few nanosheets after etching with hydrochloric acid and lithium fluoride are not well understood. Herein the structural changes induced by cationic exchange in the interlayer space of $\text{Ti}_3\text{C}_2\text{T}_z$ during washing are investigated. We also show, mostly by X-ray diffraction of $\text{Ti}_3\text{C}_2\text{T}_z$ multilayers, that cationic exchange between H_3O^+ ions, on the one hand, and Li^+ , K^+ or Mg^{2+} , on the other is occurring reversibly. The presence of Li^+ is a necessary condition for the crystalline swelling observed to $\approx 16 \text{ \AA}$, and the subsequent exfoliation of $\text{Ti}_3\text{C}_2\text{T}_z$ into single layers.

1. Introduction

Layered materials are comprised of stacked atomically thin sheets held together by forces weaker than the intraplanar forces. This feature allows for the modification of the interlayer space by the intercalation and deintercalation of molecules and/or ions. Understanding the exchange mechanism in the interlayer space is mandatory to fully understand the surface chemistry,¹ structure² and electronic properties³ of these materials. Some examples of layered materials with tuneable interlayer spaces are clay minerals, graphite and multi-layered MXenes.⁴ Discovered in 2011, MXenes are two-dimensional (2D) transition metal carbides and/or nitrides with a general formula $M_{n+1}X_nT_z$ (or $M_{1.33}XT_z$ in special cases), where M is an early transition metal, X is carbon and/or nitrogen, $n = 1, 2$ or 3 and T_z represents variable surface terminations (such as O, OH, F).^{5,6} To date, by far the most studied MXene is $Ti_3C_2T_z$. A good understanding of what occurs during its etching and subsequent washing is required to scale up the synthesis of this promising material that has shown great potential in a host of applications including energy storage,⁷ structural composites,⁸ electromagnetic interference shielding,^{9,10} and many others.^{11,12}

One of the most common ways to synthesize $Ti_3C_2T_z$ is to first selectively etch the Al layers from Ti_3AlC_2 .⁵ The multi-layered (ML) material obtained is composed of 2D titanium carbide layers that are weakly bonded to each other. If hydrofluoric acid (HF) is used to etch the Al layers,⁵ the use of an intercalant such as dimethyl sulfoxide (DMSO) is required to exfoliate the MLs into few or single layers.¹³ If the etchant is a mixture of hydrochloric acid (HCl) and lithium fluoride (LiF), there is no need for an exfoliant because after etching and during the washing steps, a spontaneous exfoliation is observed.¹⁴ In this case, colloidal suspensions with concentrations as high as 25 g.L^{-1} of 2D flakes can be obtained.¹⁵ Cations easily exchange in the interlayer space of MXenes.^{7,13,16,17} When cations intercalate the structure, they also carry

interlayer solvating water (H₂O) molecules with them. When the interlayer space (*d*-spacing) increases uniformly with the intercalation of H₂O and cations, the phenomenon, at least in the clay literature is called crystalline swelling.¹⁸

Ghidiu et al., showed that the hydration behaviour of Ti₃C₂T_z depends on the nature of the cations between the layers.¹⁶ For example, while the *d*-spacing of K⁺ intercalated MLs is mostly independent of the relative humidity and remains at 12.5 Å, the *d*-spacing of Li⁺ or Mg²⁺ intercalated MXenes increases to 16.8 Å and 15.5 Å with increasing humidity, respectively. Anions also impact the hydration behaviour; Voigt et al. showed that the presence of anions larger than F⁻ is required to observe the swelling to ≈ 16 Å.¹⁹ Typically, a *d*-spacing of 12.5 Å was attributed to a planar cationic hydration shell, and the *d*-spacing of 16.8 Å or 15.5 Å corresponds to a hydration shell where the H₂O molecules are stacked.^{16,20,21}

The focus of this work is to understand the mechanisms at the origin of the spontaneous exfoliation observed during washing after etching Ti₃AlC₂ powders with HCl/LiF solutions. In this work, we probed the nature of the interlayer cations as a function of washing cycles and chemistry of the washing solutions, by measuring the *d*-spacing using X-ray diffraction (XRD). We show that cationic exchange can explain the structural changes observed.

2. Experimental section

2.1. Sample preparation

Synthesis of Ti₃AlC₂. Ti₃AlC₂ powder was synthesized by heating a ball-mixed mixture of TiC, Al and Ti (Alfa Aesar, 99.5% purity) powders in a molar ratio of 2:1.05:1, respectively, in argon,

Ar, atmosphere at a rate of 5 °C / min to 1350 °C and holding time of 2 h. The resulting solid is milled and sieved (- 400 mesh) to obtain a powder with particle size under 38 μm.

Washing procedure. In the rest of the experimental section, a washing step consists of the following procedure: 40 mL of the washing solution is added to the MLs, the mixture is shaken for 1 min and centrifuged at 3500 rpm for 2 min. The pH of the supernatant is measured, and then discarded.

Synthesis of $Ti_3C_2T_z$ intercalated with ions. $Ti_3C_2T_z$ intercalated with Li^+ , K^+ and Mg^{2+} were synthesized following Ghidui et al. procedure.¹⁶ Here, 3.27 g of lithium chloride (LiCl) was added to 30 mL of a 10 wt.% HF solution. Then, 3 g of the Ti_3AlC_2 powders (sieved to < 38 μm) was slowly added, and the solution was left to stir at room temperature (between 20 and 25 °C) for 24 h. The resulting sediment was divided into 6 different batches and washed three times with 6 M HCl to remove unreacted LiCl, and at least three times with distilled water until the supernatant reaches a pH ~ 5. Lastly, 40 mL of aqueous salt solutions (1 M LiCl, 1M KCl, or 0.5 M $MgCl_2$) were added to the sediment. The mixtures were shaken for 2 mins and allowed to sit. After 1 h, the salt solutions were replaced with fresh ones, and the mixtures were allowed to sit for a further 24 h. After centrifugation, the sediment was washed twice with distilled water. Using this procedure, MXenes intercalated with Li^+ , K^+ or Mg^{2+} were obtained.

Different washing procedure were then implemented on these starting materials, crucially, before they were allowed to dry. Schematics of the washing procedure can be found in Figures 1 and 2. Additional washing procedures can be found in Supplementary information.

- For all the samples, the first wash (wash 1) was with a 0.5 M HCl solution. The second wash (wash 2) was with either H_2O (samples M-a, M = Li, K or Mg) or 1 M of KCl, LiCl, or 0.5

M MgCl₂ (samples M-b). In the two latter cases, a third wash was carried out (wash 3). Figure 1A shows a schematic of these steps.

- For the Energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) analyses, the same washing procedure as that shown in Figure 1A was used, except the samples washed with KCl or MgCl₂ were washed twice with water to remove unreacted salts (see Figure 2A).

Synthesis of Ti₃C₂T_z in HCl/LiF. 1.5 g of lithium fluoride (LiF, Alfa Aesar, 98% purity) was dissolved in 15 mL of 9 M hydrochloric acid (HCl, Fisher Scientific). 1.5 g of Ti₃AlC₂ (sieved to < 38 μm) was slowly added. The solution was stirred at 35 °C for 24 h. The sediment was washed 10 or 8 times with either distilled water or 0.5 M HCl, respectively. Between every washing step, X-ray diffraction (XRD) patterns were acquired on the wet sediment (Figure 3). The samples collected for XRD was then placed back in the centrifuge tube before continuing the washing procedure.

In a second experiment (Figure 5), the sediment, after etching, was washed 10 times with 0.5 M HCl. The sediment was then split in two: one part was washed four times with water, and the other part was washed four times with a 1 M aqueous LiCl solution.

2.2. Characterization techniques

XRD patterns on wet samples were acquired using a Rigaku SmartLab powder diffractometer setup in the Bragg-Brentano geometry with Cu K α radiations in the 4 – 9° 2 θ range using a 0.02° step size and a dwell time of 1 s per step. It is particularly important to ensure that the samples remain wet during the XRD acquisition, and therefore the scans durations were kept to a

minimum (5 min). No additional water was added to the sample, in order to not modify the pH of the environment. XRD patterns on dry samples were acquired using a Miniflex Rigaku diffractometer in the $4 - 80^\circ 2\theta$ range using a 0.02° step size and a dwell time of 2 s per step.

X-ray Photoelectron Spectroscopy (XPS) was performed using a VersaProbe 5000 instrument (Physical Electronics, Chanhassen, Minnesota). All samples were sputtered using an Ar-ion gun (1 kV) for 2 min. A pass energy of 23.5 eV was used for all scans, with an energy step of 0.025 eV and step time of 0.5 s. The number of repeats per scan was set to 25.

Energy dispersive spectroscopy (EDS) measurements in a scanning electron microscope (SEM) were performed on a Zeiss Supra 50VP (Carl Zeiss AG, Germany) with an acceleration voltage of 15 kV. ML powders were fixed on a carbon tape for these measurements.

3. Results and discussion

3.1. Structural changes induced by cation exchange in $\text{Ti}_3\text{C}_2\text{T}_z$

As noted above, the washing procedure after etching in HCl/LiF is typically carried out with water to remove the etchants - HCl and LiF – and any reaction by-products, such as AlF_3 . To decouple the effects of HCl and intercalated cations, we first studied the influence of HCl on the d -spacings, as a function of the latter. For this, $\text{Ti}_3\text{C}_2\text{T}_z$ MLs intercalated with Li^+ , K^+ or Mg^{2+} were synthesized using the procedure of Ghidui et al.¹⁶ A series of washing steps outlined in Figure 1 A and explained in the experimental section were then executed. XRD patterns were acquired on wet samples after washing. The results are plotted in Figure 1 B-D. The pH of the supernatant after each corresponding washing step is also reported on the figures. All patterns

focus on the (0002) peak related to the c -lattice parameter. Half of this value corresponds to the d -spacing, which is indicated on the top x -axis of all diffractograms.

The main d -spacings of the initial materials synthesized are the same as previously reported in the literature: 16.2 Å, 12.8 Å and 15.4 Å for the Li⁺, K⁺ and Mg²⁺ intercalated Ti₃C₂T_z MLs, respectively.¹⁶ For the Li-intercalated sample, a peak is also detected at 12.8 Å, implying the sample was not fully hydrated.²⁰ Interestingly, the three starting materials behave quite similarly when washed with 0.5 M HCl: the d -spacing always goes to 13.4 Å, as indicated by diffractograms labelled Mg a, K a or Li a, viz. wash 1 HCl in Figure 1 B-D. Subsequent washing with H₂O does not alter this spacing (see grey lines labelled Mg a, K a or Li a - wash 2 H₂O in Figure 1 B-D), even after two additional washes (XRD patterns not shown).

However, when the starting materials were first washed with HCl and then with salt solutions containing the initial intercalated cations, the d -spacings evolved quite differently. With Li, a distribution of d -spacings (pattern labelled Li b - wash 2 LiCl in Figure 1B) was observed between 16.2 Å and 12.8 Å, consistent with Li⁺ in the interlayer space with two and one H₂O layers, respectively.²¹ With an additional wash with 1 M LiCl, the intensity of the 16.2 Å peak increased, at the expense of the one at 12.8 Å. This additional wash clearly facilitated the hydration of the interlayer space. For K⁺, the d -spacing returns to 12.8 Å upon washing with KCl (pattern labelled K b - wash 2 KCl in Figure 1C). In the Mg²⁺ case two peaks at higher d -spacings viz. 15 and 15.4 Å are observed. An additional wash with MgCl₂ enables the MLs to fully hydrate and increase the d -spacing to 15.4 Å (patterns labelled Mg b wash 2 and 3 MgCl₂ in Figure 1D).

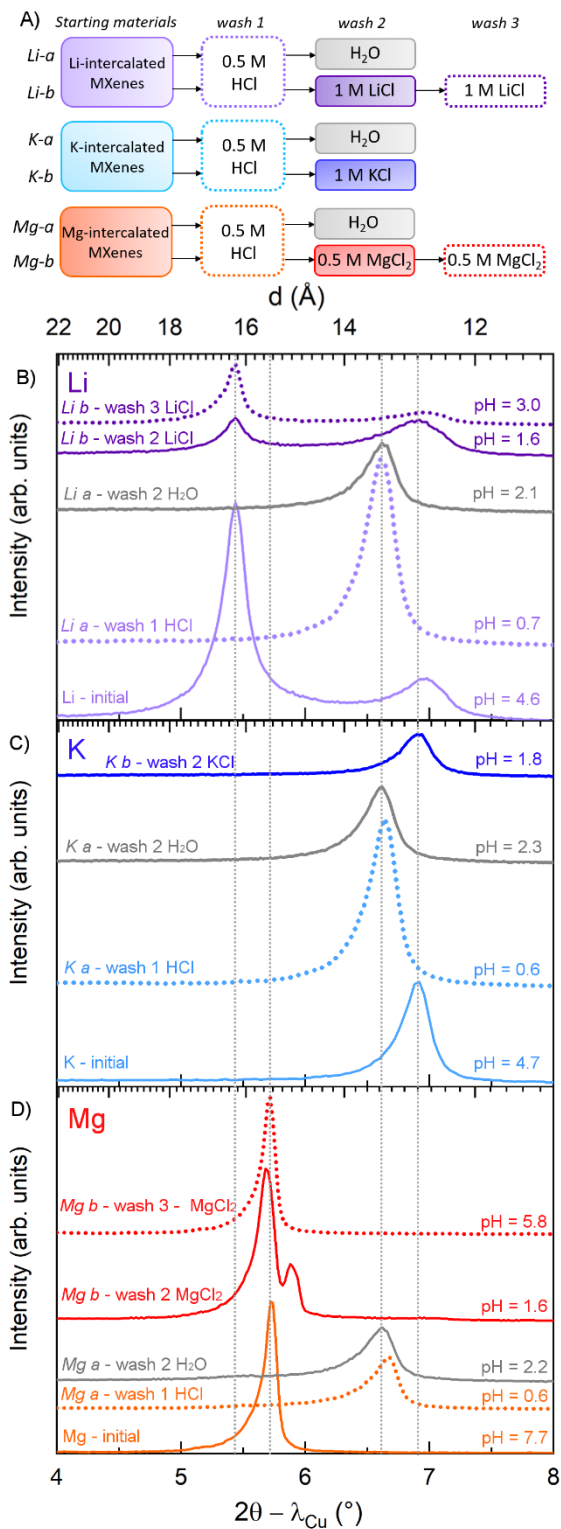


Figure 1: Influence of washing procedures on d -spacing of $\text{Ti}_3\text{C}_2\text{T}_z$ MLs intercalated with Li^+ , K^+ or Mg^{2+} . **A)** Schematic of washing procedures. **B-D)** XRD patterns on wet samples, for bottom to top for each panel: initial

materials in purple, blue or orange for MXenes intercalated with Li^+ , K^+ or Mg^{2+} , respectively; Li a, K a and Mg a samples first wash with 1 M HCl in purple, blue, and orange dotted lines, respectively (the same acquisition on b is similar); Li a, K a and Mg a samples second wash with H_2O shown by grey patterns; Li b, K b and Mg b samples second wash with salt solution of LiCl, KCl and MgCl_2 in purple, blue and red, respectively; Li b and Mg b samples third wash with salt solution of LiCl and MgCl_2 in purple and red dotted lines, respectively. The supernatant pH after each washing step is also shown.

Energy dispersive spectroscopy (EDS) in a scanning electron microscope (SEM) were performed on the K- and Mg- samples (Figure 2 and Table S1). For the measurements on samples washed with KCl or MgCl_2 solution (K b - wash 3 and Mg b - wash 3, respectively), two additional washes with H_2O were carried out to remove any un-reacted salts without modifying the *d*-spacing (Figure 2 A and B). For the HCl washed samples, neither Mg^{2+} nor K^+ was detected by EDS or after subsequent washing with H_2O (see spectra M α a - wash 1 HCl and wash 2 H_2O , M is Mg or K). For the salt washed MLs, even after the two additional H_2O washes, K and Mg were detected in the EDS spectra which confirms the re-intercalation of these elements when exposed to KCl or MgCl_2 solutions, respectively. Additional measurements on the samples with K by X-ray photoelectron spectroscopy (XPS) confirmed these results (Figure S1).

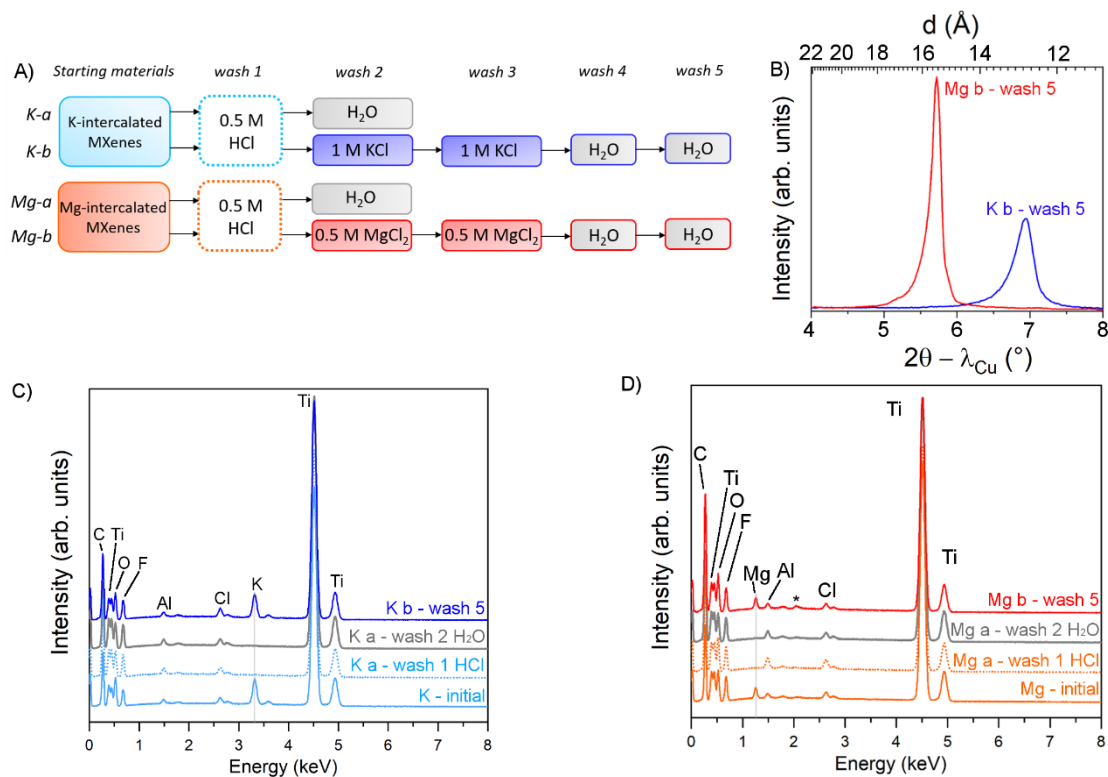


Figure 2: (A) Schematic of washing procedure, which was identical to that shown in Figure 1, except two additional washes with water were performed on the samples K-b and Mg-b after washing with KCl or MgCl₂ to remove unreacted salts. (B) XRD pattern on samples K b - wash 5 and Mg b - wash 5, the d -spacing remains at 12.5 and 15.5 Å, respectively as in K b - wash 3 and Mg b - wash 3. (C-D) EDS data for (from bottom to top): initial materials in blue or orange for MXenes intercalated with K⁺ or Mg²⁺, respectively; K a and Mg a samples first wash with 1 M HCl in blue and orange dotted lines, respectively; K a and Mg a samples after second wash with water shown by grey patterns; K b and Mg b samples after fifth wash with KCl or MgCl₂ salt solutions and then water, in blue and red, respectively. Peak indexed with a star corresponds to an unknown impurity.

The same series of experiments were repeated on K- and Mg-intercalated MLs using hydrobromic acid (HBr). The XRD and XPS results showed the same trends (Figures S2 and S3) seen when HCl was used (Figure 1). It follows that the role of anions on the d -spacings is much weaker than the cations during washing.

To summarize the results at this juncture: cation exchange between Li^+ , K^+ or Mg^{2+} , on the one hand, and H_3O^+ on the other, occurs when MLs $\text{Ti}_3\text{C}_2\text{T}_z$ are washed with HCl. This cation exchange result in a modification of the d -spacing. Similar exchanges were reported in clay minerals (such as montmorillonite),²²⁻²⁴ and layered titanates.²⁵ From the XRD and EDS data, we can conclude that a d -spacing of 13.4 Å corresponds to the presence of only H_3O^+ in the interlayer space. Further evidence that interlayer H_3O^+ is being replaced by Li^+ , K^+ or Mg^{2+} is the systematic lowering of the supernatant's pH after washing with the salt solutions, as compared to samples washed with H_2O (compare the pH value of Li, K or Mg a - wash 2 H_2O with Li, K, or Mg b -wash 2 - LiCl, KCl or MgCl_2). Here H_3O^+ leached into the bulk solution causes the observed drop in pH. This set of experiments also shows that cation exchange is a reversible process: the d -spacing of samples washed with HCl and then washed with their corresponding salt solutions return to their original value (Figure 1 B-D). It is also possible to directly exchange K^+ with Mg^{2+} , or to exchange K^+ with H_3O^+ , and then Mg^{2+} (see Figure S4 in Supporting Information). Lastly, contrary to previous reports in which one day of soaking was used to ensure complete exchange,¹⁶ herein the physical effects of cation exchange (d -spacing change) are shown to be quite rapid, < 10 min.

3.2. Structural changes during washing $\text{Ti}_3\text{C}_2\text{T}_z$ etched in HCl/LiF

We now turn our attention to the effect of washing after etching in HCl/LiF solutions. For this, XRD patterns on wet samples were acquired between every wash (Figure 3 A). Just after etching (wash 1), the d -spacing was at ≈ 13.8 Å. The peak was broad, with a full width at half maximum (FWHM) of $\Delta(2\theta) = 0.9^\circ$, which is evidence for structural disorder along the c direction.²¹ As discussed above, this position corresponds to the presence of H_3O^+ between the layers. Upon further washing with H_2O , the d -spacing increases to 16.2 Å and the FWHM decreases to

$\Delta(2\theta) = 0.4^\circ$, reflecting a strong ordering of the interlayer space. The removal of some etching by-products between the layers could help to increase the structural order. The pH increases until wash 6, and then stabilizes around pH = 4 (inset in Figure 3 A). Spontaneous delamination was observed during wash 10.

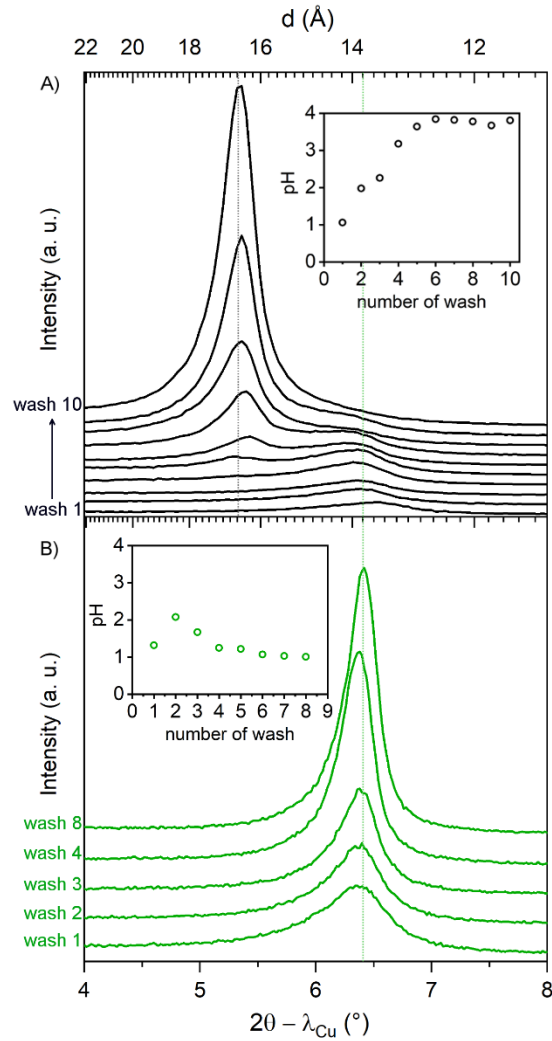


Figure 3: Effect of pH on *d*-spacing during washing Ti₃C₂T_x MLs after etching with HCl/LiF mixture. XRD patterns acquired on wet MLs between every wash with, (A) distilled H₂O, and (B) 0.5 M HCl. Insets show pH evolution of supernatant after every wash.

The bimodal distribution observed in d -spacings corresponds to a discontinuous structural expansion along c . If no cationic exchange were occurring, then washing with H_2O after etching with HCl/LiF should not alter the d -spacing. However, d increases from $\approx 13 \text{ \AA}$ to 16.5 \AA (Figure 3 A). The following hypothesis can then be made: both H_3O^+ and Li^+ are present in the interlayer space after etching, and H_3O^+ keeps the d -spacing at $\approx 13 \text{ \AA}$ (Figure 4 A). As the material is washed, cation exchange from excess salt occurs, and Li^+ substitutes H_3O^+ , enabling the interlayer space to swell to 16.5 \AA (Figure 4 B). The source of this Li is most probably, the large excess of LiF used during the synthesis ($\text{LiF}:\text{Ti}_3\text{AlC}_2 = 7.5:1$ molar ratio). Not all the Li^+ intercalates the MLs during etching, and several washing steps are needed to remove unreacted LiF . Indeed, LiF is detected by XRD on dry samples just after etching and after the first wash (Figure S5).

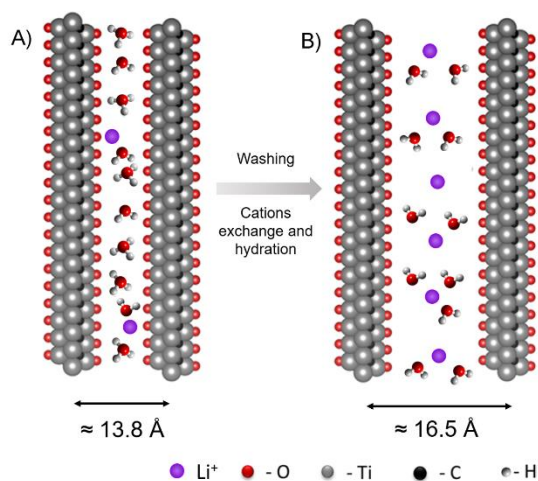


Figure 4: Schematic of effect on washing of the d -spacing of $\text{Ti}_3\text{C}_2\text{T}_z$ MLs. **(A)** After etching, both H_3O^+ and Li^+ are present between the layers. **(B)** As the MLs are washed in the presence of excess Li^+ , originating from the excess LiF used, the H_3O^+ are replaced by Li^+ , with the hydration of Li^+ , eventually leading to swelling and exfoliation to 16.5 \AA .

To further confirm this important conclusion, the MLs after etching in HCl/LiF, were washed with 0.5 M HCl instead of H₂O. The pH was maintained below 2 (Figure 3 B) and the *d*-spacing remained at $\approx 13.8 \text{ \AA}$ throughout the washing procedure. The FWHM decreased from $\Delta(2\theta) = 0.7^\circ$ to $\Delta(2\theta) = 0.3^\circ$, again indicating an increase in structural order. Since the *d*-spacing was not modified, it can be concluded that the H₃O⁺ remains in the interlayer space. Furthermore, the Li⁺ cations present after etching are probably exchanged by H₃O⁺ due to the high concentration in H₃O⁺ in the washing solution (0.5 M HCl).

After washing 10 times with 0.5 M HCl, the batch was divided into two parts as outlined in Figure 5 A. One part was washed with H₂O until a pH close to 4 was reached, and the other part was washed with a 0.5 M LiCl solution. After washing with H₂O, the *d*-spacing remained fixed at $\approx 13.8 \text{ \AA}$ (pattern labelled a - wash 14 H₂O) because no cationic exchange occurred. However, when washing with LiCl, crystalline swelling was observed to $\approx 16.8 \text{ \AA}$ at a pH as low as 2 (pattern labelled b - wash 12 LiCl). The shoulder at higher 2θ indicates a distribution of *d*-spacings. This again evidences that cationic exchange is necessary to modify the *d*-spacing. No swelling is induced when H₃O⁺ intercalated MLs are washed with H₂O, while crystalline swelling to 16.8 \AA is observed when H₃O⁺ intercalated MLs are washed with LiCl.

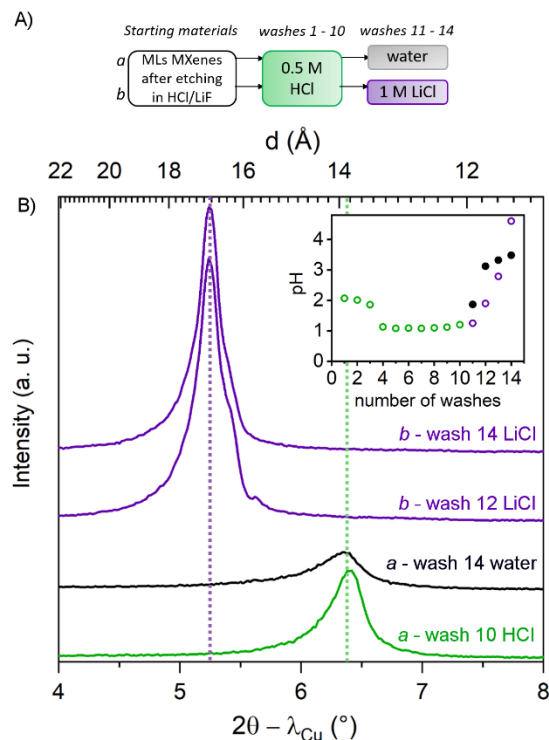


Figure 5: Influence of washing procedures on d -spacing of $Ti_3C_2T_z$ MLs etched with HCl/LiF. **A)** Summary of washing procedures. **B)** XRD patterns on wet samples, from bottom to top: a - wash 10 after 10 washes with 0.5 M HCl in green (the same acquisition on b is similar), a - wash 14 H_2O after 4 additional washes with H_2O in black, and b - wash 12 and wash 14 after 2 and 4 additional washes with 1 M LiCl in purple, respectively. Inset shows the evolution of the supernatant's pH between every wash with HCl (green open symbols), H_2O (black symbols) and 1 M LiCl (purple open symbols).

Our results provide a better understanding of several experimental procedures already reported in the literature. For example, Liu et al.²⁶ studied the impact of the nature of cations during etching Ti_3AlC_2 in different HCl/MF mixtures, where M is Li, Na, K or NH_4 . After their washing procedure, residual Li was detected on the MLs etched with HCl/LiF. However, almost no Na or K was detected after washing MLs etched in HCl/NaF or HCl/KF, respectively. Given that the solubilities of NaF and KF in water are higher than LiF, may result in the easier removal of unreacted salts during the first few washes, that in turn impeded or reduced cationic exchange

during washing. Moreover, the samples were washed several times with 2 M HCl, which probably resulted in some exchange of Na^+ and K^+ by H_3O^+ .

Voigt et al. reported a d -spacing of $\approx 13.5 \text{ \AA}$ after etching in HF and washing with H_2O in $\text{Ti}_3\text{C}_2\text{T}_z$.¹⁹ In light of our results, we can conclude that H_3O^+ ions intercalate the MLs when the etching solution is HF alone, but no cationic exchange is possible during washing and no swelling is observed. However, by washing in the presence of a cation (Li^+ in Ref.¹⁹), an exchange occurs, resulting in a d -spacing of $\approx 12.4 \text{ \AA}$ or $\approx 16 \text{ \AA}$. The latter d -spacing value is reached only if larger anions than F^- are present during etching, which enables a full hydration of the interlayer space.

4. Summary and Conclusions

Multilayered $\text{Ti}_3\text{C}_2\text{T}_z$ intercalated with different cations (Li^+ , K^+ and Mg^{2+}) were prepared and structural modifications due to cation exchange reactions were investigated. When $\text{Ti}_3\text{C}_2\text{T}_z$ MLs are hydrated with only H_3O^+ between the layers, a d -spacing of 13.4 \AA is obtained. Furthermore, cations such as Li^+ , K^+ or Mg^{2+} can reversibly substitute for H_3O^+ and for each other, with this exchange occurring in a single washing step and quite rapidly (< 10 mins). It has long been established that etching Ti_3AlC_2 powders in HF, resulted in MLs that did not spontaneously delaminate, while those etched in HCl/LiF solutions, after several washes did. The reasons for this difference in behavior have remained unclear. Using mostly XRD, and various washing procedures, we conclude that for $\text{Ti}_3\text{C}_2\text{T}_z$ MLs:

- i) Just after etching Ti_3AlC_2 with HCl and LiF, both H_3O^+ and Li^+ are present in the interlayer space. When Li^+ cations are present during washing with water (excess in etching solution), they replace their H_3O^+ counterparts and the interlayer space swells to $\approx 16 \text{ \AA}$. It is this swelling, in turn, that results in spontaneous delamination.
- ii) When washing with HCl, the interlayer space remains at $\approx 13.5 \text{ \AA}$ and dominated by H_3O^+ cations.

This work thus provides new insight on the crystalline swelling observed after washing MXenes etched in HCl/LiF mixtures. With this new understanding, even better control of both the interlayer chemistry and spacing is possible. Similar studies need to be carried out for other MXene compositions as well.

ASSOCIATED CONTENT

Supporting Information. EDS, XPS and additional XRD data referred in the article (PDF).

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Notes

The authors declare no competing financial interests.

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