Silica-Pillared Mo2TiC2 MXene for High-Power and Long-life Lithium and Sodium-ion Batteries

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Silica-Pillared Mo\textsubscript{2}TiC\textsubscript{2} MXene for High-Power and Long-life Lithium and Sodium-ion Batteries

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Abstract

In this work, we apply an amine-assisted silica pillaring method to create the first example of a porous Mo\textsubscript{2}TiC\textsubscript{2} MXene with nanoengineered interlayer distances. The pillared Mo\textsubscript{2}TiC\textsubscript{2} has a surface area of 202 m\textsuperscript{2} g\textsuperscript{-1}, which is among the highest reported for any MXene, and has a variable gallery height between 0.7 and 3 nm. The expanded interlayer distance leads to significantly enhanced cycling performance for Li-ion storage, with superior capacities, rate capabilities and cycling stabilities in comparison to the non-pillared version. The pillared Mo\textsubscript{2}TiC\textsubscript{2} achieved capacities over 1.7 times greater than multilayered MXene at 20 mA g\textsuperscript{-1} (≈ 320 mAh g\textsuperscript{-1}) and 2.5 times higher at 1 A g\textsuperscript{-1} (≈ 150 mAh g\textsuperscript{-1}). The fast-charging properties of pillared Mo\textsubscript{2}TiC\textsubscript{2} are further demonstrated by outstanding stability even at 1 A g\textsuperscript{-1} (under 8 min charge time), retaining 80% of the initial capacity after 500 cycles. Furthermore, we use a combination of spectroscopic techniques (i.e. XPS, NMR and Raman) to show unambiguously that the charge storage mechanism of this MXene occurs by a conversion reaction through the formation of Li\textsubscript{2}O. This reaction increases by 2-fold the capacity beyond intercalation, and therefore, its understanding is crucial for further development of this family of compounds. In addition, we also investigate for the first time the sodium storage properties of the pillared and non-pillared Mo\textsubscript{2}TiC\textsubscript{2}.

Introduction

Over recent years, there has been incredible growth in the research and application of Li-ion batteries, which are now widely used in portable electronics, electric vehicles and grid storage applications.\textsuperscript{1,2} However, further uptake of these technologies in more demanding applications, such as fast-charging electric vehicles and grid storage, requires significant improvements in high-rate charging and cycling lifetime, without compromising their energy density. Since these characteristics are determined by
the electrode materials, there is an urgent need to develop new materials that can satisfy these demands. Currently used negative electrodes for Li-ion batteries often suffer from poor rate capability (for example, state-of-the-art negative electrode material graphite), and those with an impressive performance at high rates cannot achieve high capacities overall (lithium titanate only has a theoretical capacity of 150 mAh g\(^{-1}\) and niobium oxides have a capacity of 200 mAh g\(^{-1}\), with both having little variation over different rates).\(^3\)–\(^5\)

Two-dimensional (2D) materials such as graphene have emerged as promising candidates for next-generation high-rate negative electrode materials due to their combination of high electrical conductivity and large 2D channels, which allow for fast electron and Li\(^+\) diffusion, facilitating fast charging times.\(^6\) However, 2D materials typically suffer from issues such as restacking of nanosheets during cycling, which can block Li diffusion channels, leading to low capacities, rate capabilities and cycling stabilities.\(^7\) It is therefore crucial to develop methods which give rise to controlled open electrode architectures that are stable even when cycled at high rates.

MXenes are an exciting family of 2D materials which have attracted significant research attention since their discovery in 2011, especially in the field of energy storage.\(^8\)–\(^11\) However, like other 2D materials, electrode architecture plays a crucial role in their electrochemical performance, with multilayered or restacked MXenes showing poor cycling performance.\(^12\),\(^13\) Titanium-based MXenes such as Ti\(_2\)C or Ti\(_3\)C\(_2\) have been by far the most heavily studied of the MXene family, despite more than 30 different MXenes having been synthesised to date.\(^14\) This is particularly important because Ti-based MXenes suffer from poor initial coulombic efficiencies (typically 40-60%), which severely limit their application in full cells.\(^15\) In 2015, Anasori et al. first reported Mo\(_2\)TiC\(_2\), an out-of-plane ordered MXene, with Mo occupying the outer metal layers, while the inner metal layer is exclusively Ti.\(^16\) This allows the effect of the outer metal element to be studied, since Mo\(_2\)TiC\(_2\) is otherwise analogous to Ti\(_3\)C\(_2\).\(^16\) Mo\(_2\)TiC\(_2\) had several promising features for Li-ion battery applications, with delaminated Mo\(_2\)TiC\(_2\) showing capacities up to 260 mAh g\(^{-1}\), an initial coulombic efficiency of 86% and low average voltage.\(^16\) Despite this, there have only been a handful of reports on this MXene,\(^16\)–\(^20\) with only one other reporting Li-ion battery performance.

Significantly, unlike Ti-based MXenes, the load curve for Mo\(_2\)TiC\(_2\) displayed a plateau below 0.6 V, suggesting a different charge storage mechanism. Computational studies implied that a conversion reaction occurs between lithiated Mo-O surface groups (formed via Li intercalation in Reaction 1) and two further moles of Li as shown by Reaction 2, boosting the capacity.\(^16\) The theoretical capacity achieved in Reaction 1 is 180 mAh g\(^{-1}\), which increases to 356 mAh g\(^{-1}\) after the proposed conversion reaction.
\[
\text{Mo}_2\text{TiC}_2\text{O}_2 + 2 \text{Li}^+ + 2 \text{e}^- \rightarrow \text{Mo}_2\text{TiC}_2\text{O}_2\text{Li}_2
\] (1)

\[
\text{Mo}_2\text{TiC}_2\text{O}_2\text{Li}_2 + 2 \text{Li}^+ + 2 \text{e}^- \rightarrow \text{Mo}_2\text{TiC}_2 + 2 \text{Li}_2\text{O}
\] (2)

The proposed mechanism is similar to the lithiation of Mo oxides, which is accompanied by large volume changes, causing significant capacity fade.\textsuperscript{21} This could explain the relatively high fade seen in previous Mo\textsubscript{2}TiC\textsubscript{2} studies,\textsuperscript{16,18} demonstrating the need to develop methods that optimise the electrode architecture and increase the cycling stability of this material. There have been no reports to-date on engineered electrode architectures for Mo\textsubscript{2}TiC\textsubscript{2} in electrochemical applications, despite the clear promise of this material. Furthermore, the lithiation mechanism for this material has not been experimentally verified yet.

Pillaring is a technique used to make porous layered materials from non-porous precursors, by inserting foreign species into the interlayer, which expands the pore space and creates stable architectures which prevent sheets from restacking.\textsuperscript{22} This technique has recently been applied to MXenes, and has been shown to improve performance in a variety of electrochemical energy storage applications such as Li, Na and Zn-ion batteries, aqueous supercapacitors and solid-state supercapacitors.\textsuperscript{23–30} However, these reports have been limited to titanium MXenes, with none of these techniques applied to the wider MXene family.

In this work, we developed a porous Mo\textsubscript{2}TiC\textsubscript{2} architecture using an amine-assisted pillaring technique (Figure 1) and obtained the largest BET surface area reported for any Mo-based MXene to-date. We tested the resulting pillared Mo\textsubscript{2}TiC\textsubscript{2} for Li-ion storage, and obtained significantly enhanced electrochemical performance, with superior capacities, rate capabilities and cycling stabilities compared to the non-pillared version. Furthermore, the charge compensation mechanism in Mo-based MXenes was investigated for the first time using a combination spectroscopic techniques, including NMR, XPS and Raman. We believe that these studies are crucial for the further development of this class of MXene materials as electrode materials in Li-ion batteries for high-rate and long-life applications. In addition, due to the growing importance of Na-ion research as a promising low-cost alternative to lithium-ion batteries, we also report for the first time results for the use of Mo\textsubscript{2}TiC\textsubscript{2} in Na-ion half-cells.
**Figure 1.** Schematic representation of the amine-assisted silica pillaring method. Inset (dashed green box) illustrates the crystal structure of the out-out-plane ordered MXene Mo$_2$TiC$_2$.

**Results**

**MAX phase and MXene synthesis**

The Mo$_2$TiAlC$_2$ MAX phase was synthesised following previously reported methods, with details given in the experimental section.$^{16,31}$ The powder X-ray diffraction (PXRD) data matches previous reports, showing the successful synthesis of Mo$_2$TiAlC$_2$ (Figure 2).$^{16}$
To avoid the handling of HF, the synthesis of Mo$_2$TiC$_2$ was done for the first time using an adapted version of the LiF-HCl method which has been successfully used for titanium-based MXenes.\textsuperscript{32} Details of this can be found in the experimental section. PXRD data are in agreement with previously reported diffraction data for Mo$_2$TiC$_2$\textsuperscript{16} demonstrating that the Mo$_2$TiC$_2$ MXene was successfully etched using the described method (Figure 2a). The (002) diffraction peak of Mo$_2$TiC$_2$ has shifted to a lower angle compared to the MAX phase (to ca. 7° 2θ), and has increased in intensity, as expected from the formation of a MXene phase.\textsuperscript{33} A small peak at 9.5° 2θ, which corresponds to the (002) diffraction peak of Mo$_2$TiAlC$_2$, indicates that a minimal impurity corresponding to the MAX phase remains. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were also carried out to further confirm the formation of the Mo$_2$TiC$_2$ MXene. SEM micrographs show the layered morphology typical of an MXene in the etched material, with some opening up between the layers also visible.
(Figure 2b). The flakes have lateral dimensions in the range of 1-10 μm, with thickness between 1 and 5 μm, which are similar in size to other reported MXenes, including Mo2TiC2. EDS analysis shows that the MXene-like flakes contain no Al, demonstrating successful etching of the MAX phase and that Mo2TiC2 is terminated with –O and/or -OH groups (9.3 wt.%) and –F groups (1.5 wt.%), akin to its Ti3C2 counterpart (Figure S1). The MXene has a formula of Mo2TiC2O1.75F0.25, which is consistent with the literature.

Having confirmed the successful synthesis of the Mo2TiC2, we then applied our previously reported amine-assisted SiO2 pillaring method to this MXene (see experimental section). Throughout the paper, we refer to Mo2TiC2-Si as the pillared sample intercalated with dodecylamine (DDA) and tetraethyl orthosilicate (TEOS) and Mo2TiC2-Si-400 as the pillared sample after calcination at 400 °C (Figure 1).

PXRD data shows a clear shift in the (002) diffraction peak of Mo2TiC2-Si to 2.2° 2θ, demonstrating intercalation (Figure 2c). This gives a d-spacing of just under 4 nm, corresponding to a gallery height of around 3 nm, larger than any that have been reported for other layered Mo-based materials such as Mo2C and MoS2 (Table S1). In addition to the peaks around 2.2° 2θ, a small diffraction peak at 4.9° 2θ, corresponding to a d-spacing of 1.8 nm, is also visible, which is assigned as the (004) diffraction peak, further confirming the enlarged interlayer distance. After calcination (Mo2TiC2-Si-400), the (002) diffraction peak shifts to a higher angle to 4.5° 2θ (Figure 2c and 2d), corresponding to a d-spacing of around 2 nm, which gives a gallery height of 1 nm. The shift suggests that the DDA template is successfully removed, which is also supported by the loss of peaks corresponding to DDA in the Raman spectra (Figure S3). SEM studies (Figure 3) also confirm the layered morphology of the MXene is retained after calcination, while EDS results demonstrate significant Si content (3.2 wt.%) in the final material (Figure S4). The Si does not form clusters across the MXene flake, and surface crystals of SiO2 are not visible. This supports the formation of SiO2 pillars between the MXene layers, which is further demonstrated by careful inspection of the elemental distribution map for Si (Figure 3b and 3c), which reveals banding in the Si concentration. Direct comparison with the SEM micrograph (Figure 3a) demonstrates that the areas of high Si concentration correspond to areas between the Mo2TiC2 sheets, while areas of low concentration correspond to the location of the MXene sheets.

BET analysis using a nitrogen isotherm at 77 K showed that the pillaring procedure resulted in a substantial increase in BET specific surface area, with the pillared Mo2TiC2 MXene obtaining a surface area of 202 m² g⁻¹ compared to around 8 m² g⁻¹ for the non-pillared material (Figure 3e). This is one of the largest surface areas reported for any MXene, and the largest for a non-Ti based MXene. Additionally, this is also larger than previously reported results for pillared MoS2 (Table S1).
size distribution analysis on the pillared MXene demonstrated the existence of pores just over 1 nm in size (Figure S5), in close agreement with the PXRD data (Figure 2d), supporting the presence of large interlayer pores in the pillared MXene.

Figure 3. a) SEM micrograph of Mo$_2$TiC$_2$-Si-400 MXene after calcination at 400 °C for 5 h under flowing argon. b) and c) EDS maps showing the Si distribution in the pillared MXene, with the green dotted lines in a) and c) highlighting the Si-poor (MXene sheet) and Si-rich (interlayer) regions. d) N$_2$ adsorption-desorption curves at 77 K for the pillared and non-pillared Mo$_2$TiC$_2$.

To further investigate the structure of the synthesised Mo$_2$TiC$_2$ and the effect of the pillaring process on the MXene, X-ray photoelectron spectroscopy (XPS) was used to study the Mo, Ti and O valence states in the as-made and pillared MXene, and Si was also studied in the pillared material. Figure 4 shows the Mo 3d XPS spectra for the non-pillared and pillared Mo$_2$TiC$_2$. There are three main peaks visible in both samples centred at 229.8, 233.0 and 236.0 eV for Mo$_2$TiC$_2$ and 229.7, 232.9 and 236.1 eV for Mo$_2$TiC$_2$-Si-400. These peaks are in good agreement with a previous report on Mo$_2$TiC$_2$ Mo 3d XPS spectra, supporting successful Mo$_2$TiC$_2$ synthesis.$^{17}$ It is known that the large peaks at around 229.8 and 233.0 eV correspond to the electrons in the 3d$_{5/2}$ and 3d$_{3/2}$ levels for the expected MXene Mo environment (Mo-C), which indicates that 4+ is the dominant oxidation state. The small peak at
236.0 eV corresponds to surface Mo oxides, (Mo$^{6+}$, 3d$_{3/2}$ electrons) showing that, like titanium-based MXenes, Mo$_2$TiC$_2$ also undergoes a slight surface oxidation either during the etching process or when exposed to ambient conditions. The Mo$^{6+}$ 3d$_{5/2}$ electrons contribute to the peak centred around 233.0 eV, with an expected binding energy of 232.7 eV. The presence of a small amount of these surface oxides has also been reported previously for Mo$_2$TiC$_2$, where HF etching was used. The surface oxide peaks do not appear to grow after pillaring and calcination, suggesting that the Ar atmosphere during calcination was sufficient to avoid extra MXene oxidation. Ti 3d XPS spectra (Figure 4c and S5) follows the same pattern, with 3+ being the dominant oxidation state and some Ti$^{4+}$ oxides also being present.

**Figure 4.** Mo 3d XPS spectra for a) non-pillared Mo$_2$TiC$_2$ and b) Mo$_2$TiC$_2$-Si-400 after calcination at 400 °C, Mo$_2$TiC$_2$-Si-400. c) Ti 2p XPS spectra of Mo$_2$TiC$_2$-Si-400. d) O 1s spectra of non-pillared Mo$_2$TiC$_2$. e) O 1s spectra of the pillared MXene Mo$_2$TiC$_2$-Si-400. f) Si 2p spectra of the pillared MXene Mo$_2$TiC$_2$-Si-400.

XPS results for the O 1s scans are shown in Figure 4d and 4e, where clear differences between the non-pillared and pillared Mo$_2$TiC$_2$ can be observed. The spectrum for the non-pillared Mo$_2$TiC$_2$ MXene matches previous reports and shows a very broad asymmetric peak which is comprised of a variety of components as a result of multiple oxygen-containing species being present in the sample. Deconvolution reveals a component centred around 530.5 eV, which corresponds to the formation of Mo and Ti oxides, supporting the Mo 3d and Ti 2p spectra. The peak at 531.0 eV corresponds to Mo-O groups, while the peak around 532.0 eV reveals the presence of Mo-OH termination groups. At 534.0 eV there is a small component which corresponds to surface-bound H$_2$O molecules.
pillaring and calcination, there is a significant new broad peak centred around 533.2 eV, which is a result of oxygen in silica - the pillar.\textsuperscript{44} There is a substantial decrease in the component relating to -OH surface groups. Before pillaring, the OH:O ratio is approximately 2:1, as can be seen in 4d, but decreases significantly to 1:1 after pillaring (4e), demonstrating the direct involvement of the -OH groups in the pillaring process, as we have reported in our previous work for Ti\textsubscript{3}C\textsubscript{2}.\textsuperscript{34} Finally, the Si 2p XPS spectra for Mo\textsubscript{2}TiC\textsubscript{2}-Si-400 (Figure 4f) shows a broad peak at 103.9 eV, which is consistent with SiO\textsubscript{2} being the pillar.\textsuperscript{44}

Overall, these results imply that the amine-assisted pillaring method is unaffected by the change in metal in the surface layer of the MXene, and is directly applicable to Mo-based MXenes. This suggests that the pillaring method can be applied to other types of MXenes, so long as –OH surface groups are present.

**Electrochemical Testing in a Li-ion battery**

To demonstrate the advantages of the pillared structure, the Mo\textsubscript{2}TiC\textsubscript{2} materials were tested in Li-ion half-cells against Li metal, which acts as a counter and reference electrode. Figure 5 shows galvanostatic cycling data in a voltage window of 0.01-3 V vs. Li\textsuperscript{+}/Li at a rate of 20 mA g\textsuperscript{-1}. The first cycle capacities for the pillared MXene are 473 and 314 mAh g\textsuperscript{-1} on the discharge and charge respectively (Figure 5b), which are larger than for the non-pillared MXene (344 and 219 mAh g\textsuperscript{-1} respectively, Figure 5a), and previously reported Mo\textsubscript{2}TiC\textsubscript{2} (Table S2).\textsuperscript{16,18} The low coulombic efficiency of ca. 66% in the first cycle is commonly observed in MXenes and is attributed to SEI formation and irreversible reactions between surface groups and Li\textsuperscript{+} ions.\textsuperscript{45,46} The coulombic efficiency in the second cycle is 94% and this reaches ca. 99% after 18 cycles in both MXenes. Around 80% capacity is retained between the 2\textsuperscript{nd} (316 mAh g\textsuperscript{-1}) and 94\textsuperscript{th} (250 mAh g\textsuperscript{-1}) cycles in the pillared MXene (Figure 5d). By contrast, 54% capacity retention under the same conditions was observed for the as-made Mo\textsubscript{2}TiC\textsubscript{2}. Chen et al. reported a capacity of only 52 mAh g\textsuperscript{-1} by the 100\textsuperscript{th} cycle in their tests on Mo\textsubscript{2}TiC\textsubscript{2},\textsuperscript{4} which further demonstrates the remarkable improvement in cycling stability afforded by the pillaring technique reported here.

Rate capability tests were carried out at increasing rates of 20, 50, 200, 500, and 1000 mA g\textsuperscript{-1} with five discharge-charge cycles at each rate (Figure 5c). The pillared material shows superior performance at all rates, delivering discharge capacities of 312, 281, 229, 182 and 143 mAh g\textsuperscript{-1}, respectively. When the current was returned to 20 mA g\textsuperscript{-1}, the capacity was recovered to 292 mAh g\textsuperscript{-1}. In comparison, the non-pillared Mo\textsubscript{2}TiC\textsubscript{2} material delivered capacities of 205, 162, 108, 79 and 59 mAh g\textsuperscript{-1} at the respective rates, with 172 mAh g\textsuperscript{-1} recovered at 20 mA g\textsuperscript{-1}. Notably, the enhancement in capacity between the pillared and non-pillared MXene increases with rate, with the pillared MXene delivering capacities
around 1.7 times greater than for the non-pillared MXene at 20 mA g\(^{-1}\), and around 2.5 times greater than for the non-pillared MXene at 1 A g\(^{-1}\). This demonstrates that the increased interlayer spacing afforded by the pillaring enables fast Li-ion transport, resulting in superior capacities at higher rates.

**Figure 5.** Galvanostatic charge-discharge testing of Mo\(_2\)TiC\(_2\) samples in Li-ion half-cells in a voltage range of 0.01-3 V vs. Li\(^+\)/Li. a) Load curves for selected cycles of Mo\(_2\)TiC\(_2\). b) Load curves for selected cycles of Mo\(_2\)TiC\(_2\)-Si-400. c) Rate capability testing at 20, 50, 200, 500, 1000 mA g\(^{-1}\) for 5 cycles at each rate for the pillared (blue) and non-pillared (red) samples. d) Cycling stability data and coulombic efficiencies over 94 cycles for the pillared (blue) and non-pillared (red) samples. e) Long-term high-rate cycling stability of Mo\(_2\)TiC\(_2\)-Si-400 at 1 A g\(^{-1}\) over 500 cycles.
Since the pillared MXene showed impressive capacity at high rates, its high-rate cycling stability was then tested by continuous galvanostatic cycling at 1 A g\(^{-1}\) (corresponding to a charging/discharging time of 8 min) after the rate capability test. After 500 cycles at 1 A g\(^{-1}\), it retained a capacity of 108 mAh g\(^{-1}\), a capacity retention of 80% compared to the 1\(^{st}\) cycle (135 mAh g\(^{-1}\)), (Figure 5e). The average coulombic efficiency over these cycles was close to 100%, indicating highly reversible charge storage at this rate. This shows that Mo\(_2\)TiC\(_2\)-Si-400 is a very stable electrode, making it highly suitable for high-power and long-life batteries. In addition, a comprehensive comparison of our work with other Mo-based MXenes for lithium-ion battery applications demonstrates the superior performance of our pillared Mo\(_2\)TiC\(_2\) (Figure 6 and Table S2).

![Graph](image.png)

**Figure 6.** Rate capability comparison of the performance of the Mo\(_2\)TiC\(_2\) MXenes reported in this work with existing reports of Mo-based MXenes electrodes supported on Cu current collectors for lithium-ion batteries: Mo\(_2\)TiC\(_2\) (HF),\(^{16}\) d-Mo\(_2\)TiC\(_2\) (HF)\(^{18}\) and mesoporous Mo\(_2\)C\(^{47}\).

The load curves for both materials (i.e. pillared and non-pillared) display very similar features and are markedly different from titanium-based MXenes, which typically display very linear profiles.\(^{48}\) The Mo\(_2\)TiC\(_2\) load curves display two clear regions on discharge after the first cycle, the first of which is between 3 and 0.6 V, which slopes with a linear profile and a second region between 0.6 and 0.01 V where there is a sloping plateau feature appearing, demonstrating that a different charge storage mechanism operates in this region. Closer inspection of the load curves reveals that the majority of the capacity is stored in the region below 0.6 V (215 mAh g\(^{-1}\) for the pillared material on the 2\(^{nd}\) cycle),
but that the capacity fade also occurs mostly in that region (160 mAh g\(^{-1}\), 73%, is retained after 94 cycles). This capacity loss is even more dramatic in the non-pillared MXene, where the sloping plateau feature is substantially reduced during cycling to just 90 mAh g\(^{-1}\) after 94\textsuperscript{th} cycles (53% retention). Furthermore, differential dQ dV\(^{-1}\) plots of both non-pillared and pillared samples (Figures S7 and S8) show a peak at 0.6 V, which rapidly decreases with cycling, confirming that this low voltage process contributes significant to the capacity during the initial cycles but it is a significant cause of capacity fade over prolonged cycling.

Anasori et al. used DFT to predict that the 0.6 V feature present in the load curves of Mo\(_2\)TiC\(_2\) could result from a conversion reaction between Mo-O groups on lithiated Mo\(_2\)TiC\(_2\)O\(_x\) (formed by Li intercalation between 3 and 0.6 V) and extra Li moles to form Li\(_2\)O\(_x\).\(^{16}\) Li\(_2\)O is known to be a poor electrical conductor, and it is possible that its formation, which in transition metal oxide electrodes is often poorly reversible and accompanied by a large volume change, is the main cause of the capacity fade seen in these electrodes, with several bulk oxides reporting capacity retentions between 40-50% over 100 cycles.\(^{49}\) Therefore, we used a series of ex-situ spectroscopic studies to experimentally validate the charge storage mechanism for the first time.

To study the reactivity of the SiO\(_2\) pillars, we combined \(^{29}\)Si NMR and Si 2p XPS data to investigate any potential lithiation of the pillars, both in the bulk and near the surface of the pillared MXene. \(^{29}\)Si solid-state NMR (Figure 7c) revealed that there is only one Si environment present within the pristine pillared MXene structure, which matches well with the expected chemical shift for SiO\(_2\) (i.e. -108 ppm).\(^{50}\) There is no change in the \(^{29}\)Si NMR environment after discharge or subsequent charge, confirming that the SiO\(_2\) pillars are stable during cycling, and that no alloying reaction occurs. This is supported by ex-situ Si 2p XPS (Figure 7d), which also shows no significant changes in the spectra at different states-of-charge, suggesting no difference in redox activity between bulk and near-surface pillars. Additionally, no signal corresponding to Li\(_x\)Si\(_y\) alloys (expected between 20 and 10 ppm) could be distinguished in the \(^{7}\)Li NMR spectra (Figure S9).\(^{50,51}\) Significantly, this means that the improved electrochemical performance seen in the pillared Mo\(_2\)TiC\(_2\) is a result of the enlarged interlayer spacing, and not due to the lithiation of SiO\(_2\).

Ex-situ O 1s XPS analysis was used to investigate the proposed mechanism of reversible Li\(_2\)O formation in Mo\(_2\)TiC\(_2\) (Figure 7b). At OCV there is just one broad peak visible, which is centred on 532.0 eV. Deconvolution reveals that there are two main components to this peak at 531.7 eV (assigned to the carbonate oxygen from the electrolyte)\(^{52}\) and 530.6 eV (which matches the Mo-Ox environment present in the powdered material in Figure 4). There is little change in these two peaks upon cycling,
with the shifts varying less than 0.2 eV at all states-of-charge. However, the spectrum for the electrode discharged to 0.01 V shows a new peak at 528.6 eV, which matches well with Li$_2$O.$^{44}$ Upon charging to 3 V, this peak disappears, confirming that Li$_2$O is reversibly formed and removed upon lithiation (discharging) and delithiation (charging) in the pillared material.

Figure 7. Ex-situ MAS NMR spectra (16.4 T, 30 kHz MAS) and XPS spectra of Mo$_2$TiC$_2$-Si-400 at selected states-of-charge. a) Schematic illustrating the lithiation mechanism for oxygen-terminated Mo$_2$TiC$_2$, with the MXene sheets shown in blue and the pillars in orange. b) Ex-situ O 1s XPS spectra. c) Ex-situ $^{29}$Si MAS NMR spectra. d) Ex-situ Si 2p XPS spectra.

Ex-situ solid-state NMR was then used to study the evolution of the local structure of the H, Li, F environments within the bulk of the pillared MXene upon cycling. $^1$H NMR showed a broad peak present in the pristine sample, which is assigned to $^1$H environments in the polyvinylidene fluoride (PVDF) binder (Figure S10).$^{53}$ After discharge to 0.01 V, new peaks appear at 3 and 4 ppm, which correspond to carbonate environments originating from retained electrolyte solvent molecules in the material.$^{53}$ In addition, a new peak at -1.5 ppm is now present, which can clearly be assigned as LiOH based on previous reports.$^{53}$ This peak disappears after charging to 3 V, suggesting that, like Li$_2$O, the formation of LiOH is reversible, which implies that LiOH is also a discharge product.
Overall, these results support the mechanism proposed by Anasori et al (Reactions 1 and 2), but imply that an additional reaction involving the formation of LiOH, most likely via a conversion reaction with terminal -OH groups, may also occur (Reaction 3).

\[
\text{Mo}_2\text{TiC}_2(\text{OH})_2 + 2 \text{Li}^+ + 2 \text{e}^- \rightarrow \text{Mo}_2\text{TiC}_2 + 2 \text{LiOH}
\]

(3)

This reaction could explain the second low voltage discharge peak observed in the dQ dV plots for both the non-pillared and pillared Mo2TiC2 (Figures S7 and S8). An analogous conversion reaction involving the formation of LiOH has been previously observed on RuO2. Comparing the stoichiometries of Reactions 1 and 2 with reaction 3 suggests that -OH groups may only provide half as much capacity as -O groups.

Ex-situ Raman spectroscopy supports the proposed conversion reactions (Figure S11), showing a reduction in the intensity of the Mo-O Raman modes at 170 and 270 cm\(^{-1}\) after discharging to 0.01 V, suggesting the cleavage of these bonds. It should be noted that some partial re-oxidation is expected, which may explain the continued presence of the 260 cm\(^{-1}\) Raman mode. However, LiOH is also known to have a minor Raman mode at 270 cm\(^{-1}\), and thus, it could be contributing to the 260 cm\(^{-1}\) peak. LiOH is also known to have a major Raman mode at 320 cm\(^{-1}\), which could explain the increase in intensity in this region after discharge. However, these modes cannot be conclusively assigned due to the overlap with potential MXene peaks. After discharge, a new mode at ca. 550 cm\(^{-1}\) matches previous reports for Li2O, supporting the formation of Li2O as a discharge product.

Therefore, these results could support the proposed conversion reaction mechanism whereby the -O and -OH surface functional groups of MoTiC2 MXene react with Li to form Li2O and LiOH respectively. Crucially, the Raman spectra confirm that the MXene bonding framework between Mo, C and Ti is unchanged upon cycling despite the conversion reactions unlike with transition metal oxides. This should ensure superior reversibility during the lithiation process of Mo-based MXenes compared to the metal oxides.

\(^7\)Li NMR (Figure S12) shows a broad asymmetric peak centred at -0.6 ppm. Deconvolution of this peak using a Lorentzian profile shape for the pristine sample reveals two main environments, the largest of which is assigned as pre-intercalated Li as a result of the LiF-HCl etching method used. A minor peak to the right of this, centred around -1.1 ppm, can be assigned as LiF from the etching stage, which is confirmed as being present in the structure by \(^19\)F NMR and \(^7\)Li-\(^19\)F HETCOR NMR (Figure S13). Upon discharge to 0.01 V, the broad peak shifts to a higher chemical shift (centred at -0.1 ppm), with asymmetry now present on the left side of the peak. This reveals the existence of new Li environments, which are likely to be Li2O and LiOH based on the previously discussed XPS (Figure 7b) and \(^1\)H NMR (Figure S10) data and the relative shifts compared to LiF (3-4 ppm higher than the LiF component).
However, the broad profile of the signal, resulting from the slightly disordered nature of MXenes and the lack of separation between the $^7$Li chemical shift of the different environments,\textsuperscript{54,55} means that the environments cannot be unambiguously distinguished in the broad spectra obtained using $^7$Li NMR. Nevertheless, the $^7$Li NMR spectra appear to support the XPS and $^1$H NMR results, confirming the contribution of conversion reactions to the charge storage mechanism. After charging, these changes are reversed, which demonstrates the reversible (de)lithiation of the Mo$_2$TiC$_2$ MXene.

Cyclic voltammetry was used to investigate the reactions and kinetics of the system in more detail. Figure S14 shows the cyclic voltammograms for five cycles collected at a scan rate of 0.2 mV s$^{-1}$ between 0.01-3 V vs. Li$^+/\text{Li}$. Both the non-pillared and pillared MXenes display similar CV features, with small cathodic redox peaks observed at 1.7 and 1.3 V and a large peak below 0.6 V. Above 0.6 V, the voltammograms are fairly rectangular for both materials, indicative of a capacitive-like contribution to the charge storage in this voltage range. On the first cycle, some additional cathodic peaks are observed on discharge at 1.75 and 0.7 V, while the feature below 0.6 V is also more pronounced than on subsequent cycles. These match the extra features observed in the load curves on the first discharge, and are ascribed to irreversible reactions such as SEI formation and Li trapping.\textsuperscript{45,46} This helps explain the large initial irreversible capacity loss present in the load curves on the first cycle (Figure 5).\textsuperscript{45,46} After the first cycle, the shape of the CV plots do not notably change, apart from a clear decrease in the current below 0.6 V for the non-pillared material, demonstrating the greater fade observed in this material compared to the pillared MXene, which agrees well with the GCD tests (Figure 5). The large peak below 0.6 V on discharge and the clear peak at 1.3 V on charge also match well with the plateaus observed on the load curves (Figure 5) and dQ dV$^{-1}$ plots (Figure S8) and with previous reports on Mo$_2$TiC$_2$.\textsuperscript{16}

To investigate the kinetics of the system in more detail, the cells were then cycled at increasing scan rates of 0.5, 2 and 5 mV s$^{-1}$ (Figure S15). As the scan rate increases, both materials show no major changes, with only broadening and small shifts of their redox peaks to lower voltages, suggesting that the majority of the redox reactions are kinetically favoured. The voltammograms ran at 5 mV s$^{-1}$ is much more rectangular in shape for the Mo$_2$TiC$_2$-Si-400 compared to the non-pillared Mo$_2$TiC$_2$, with increased current above 1 V. This is indicative of a greater contribution from capacitive charge storage as a result of the higher interlayer spacing and surface area in the pillared MXene, and explains the enhanced high-rate performance of this material.

This is further supported by analysing the proportion of diffusion-limited (battery-like) and surface-limited (capacitive-like) processes to the overall current. It is well known that the relationship between current and scan rate is proportional to the power half when current is diffusion-limited, whereas the
relationship is linear (power of 1) when current is surface-limited. This allows the formation of a simple power law to determine the proportion of current arising from diffusion or surface limited processes in a mixed mechanism system, as shown by Equation 4, where $i$ is current, $v$ is scan rate and $a$ and $b$ are fitting parameters. Plotting the log of the current against the log of the scan rate gives a straight line with a gradient of $b$, allowing the proportion of diffusion ($b=0.5$) or surface ($b=1$) limited current to be quantified.

$$i = av^b$$

When this analysis is carried out at different voltages, the relative contribution of these processes can be studied across the voltage window on the charge and discharge sweeps (Figure S15c and S15d). For both materials, the $b$-values are much closer to 1 (capacitive current) at higher voltages, but much closer to 0.5 (diffusion-limited battery-like processes) at low voltages (below 0.6 V). This is expected from the CV shapes, which are more rectangular at higher voltages, with prominent redox peaks present at voltages below 0.6 V. At higher voltages, the pillared Mo$_2$TiC$_2$ has a higher $b$-value (i.e. 0.86) than the non-pillared MXene (0.6-0.8) indicating an increased capacitive contribution to the charge storage resulting from the larger surface area, as previously discussed. In contrast, at low voltages, for example, 0.01 V, the pillared Mo$_2$TiC$_2$ has a lower $b$-value (0.56) than the non-pillared Mo$_2$TiC$_2$ (0.68), which indicates a greater contribution from battery-like processes at these voltages. This suggests that pillaring leads to increased charge storage contribution from the Li$_2$O conversion reaction, which explains the substantial increases in capacity compared to the non-pillared MXene.

**Electrochemical performance in a sodium-ion battery**

Following the promising performance of the Mo$_2$TiC$_2$ MXene in a Li-ion system, the non-pillared and pillared materials were further tested as Na-ion electrodes in a Na half-cell. Mo$_2$TiC$_2$ has so far not been reported as an electrode for Na-ion batteries. It can be seen that pillaring substantially improves the electrochemical performance, with a 2$^{nd}$ cycle discharge capacity of 109 mAh g$^{-1}$ compared to 74 mAh g$^{-1}$ for the non-pillared material (Figure 8). By the 80$^{th}$ cycle, the non-pillared MXene had retained a capacity of just 48 mAh g$^{-1}$ (65% capacity retention compared to the 2$^{nd}$ cycle) compared to 82 mAh g$^{-1}$ for the pillared MXene (75% capacity retention). At higher rates (Figure 8d), the pillared MXene has superior capacities compared to the non-pillared material at each rate studied, retaining 40 mAh g$^{-1}$ at 1 A g$^{-1}$, compared to 16 mAh g$^{-1}$ for the non-pillared MXene. These capacities are much lower than what was observed for the Li-ion system and correspond to a discharge product of approximately
Mo$_2$TiC$_2$O$_2$Na (theoretical capacity = 90 mAh g$^{-1}$), suggesting insertion of one mole of Na per formula unit, even in the pillared MXene. Unlike in the Li-ion system, differential dQ dV$^{-1}$ plots show no peaks which would correspond to a conversion reaction for either the pillared or non-pillared Mo$_2$TiC$_2$ (Figure S16). This suggests that, by analogy to the Li-ion system, Na$_2$O does not form in the Na-ion system, which is in agreement with the DFT studies of Anasori et al.$^{16}$

**Figure 8.** Galvanostatic discharge-charge voltage profiles of Mo$_2$TiC$_2$ samples in Na-ion half-cells in the potential range of 0.01-3 V vs. Na$^+/Na$ at 20 mA g$^{-1}$. a) Load curves for selected cycles of Mo$_2$TiC$_2$. b) Load curves for selected cycles of Mo$_2$TiC$_2$-Si-400. c) Cycling stability data and coulombic efficiencies over 80 cycles for the pillared (blue) and non-pillared (red) Mo$_2$TiC$_2$ samples. d) Rate capability tests for the pillared (blue) and non-pillared (red) Mo$_2$TiC$_2$ samples at increasing rates of 20, 50, 200, 500 and 1000 mA g$^{-1}$ for five cycles each.

These findings explain the differences in the behaviour of Mo$_2$TiC$_2$ in the Li and Na-ion systems. In the Li-ion system, at low voltages the conversion reaction to Li$_2$O provides a large amount of extra capacity. In contrast, no such conversion reaction occurs in the Na-ion systems, which leads to improved cycling stability (especially in the non-pillared materials), but with capacities around a third of the Li-ion system, even when pillared. CV analysis at different rates reveals that a much greater proportion of the current is surface controlled (capacitive) compared to the Li-ion system (Figure S17),
for example Mo$_2$TiC$_2$-Si-400 has a $b$-value of 0.73 at 0.01 V in the Na-ion system, but 0.56 in the Li-ion system at the same voltage. In the Na system, at voltages above 1 V, the $b$-value for the pillared material is around 0.9, showing that capacitive contributions dominate at higher voltages. This leads to reasonable rate capability (Figure 8d), with over 40 mAh g$^{-1}$ being retained even at the high rate of 1 A g$^{-1}$, which is higher than any other report for Mo-based MXenes in Na-ion systems (Table S3).

**Conclusions**

Overall, we demonstrate the application of an amine-assisted pillaring method to create porous Mo$_2$TiC$_2$. This leads to a large increase in interlayer spacing, achieving $d$-spacings up to 4.2 nm. This corresponds to a gallery height (pore size between layers) of around 3 nm before calcination, which is by far the largest for a Mo-based MXene, and larger than any reports found for other Mo-based layered materials such as MoS$_2$. This suggests that the amine-assisted silica pillaring method could be applied to a wide range of MXenes, and perhaps other layered materials, as long as there are sufficient –OH groups present on the surface to bind to the amine. Calcination removes the DDA template and reduces the gallery height to a still expanded 0.75 nm in the final pillared material.

When tested as the negative electrode in a lithium-ion battery, the pillared material showed significantly improved electrochemical performance with respect to the non-pillared material, reaching capacities of up to 316 mAh g$^{-1}$ (89% of the reported theoretical capacity, i.e. 356 mAh g$^{-1}$) based on two moles of Li$^+$ intercalating per formula unit followed by two further moles of Li undergoing the conversion reaction), which is the highest capacity reported so far for Mo$_2$TiC$_2$. Pillaring not only increases the capacity of the MXene, but also the cycling stability by providing free space for the reversible formation of Li$_2$O and extra intercalation of Li ions without allowing layers to restack. In addition, the rate capability is also significantly enhanced, since the enlarged interlayer spacing aids the Li$^+$ diffusion to the MXene active site. The pillared material shows high coulombic efficiency (ca. 100%) and good stability even at a high rate of 1 A g$^{-1}$ (under 8 min charge time) returning 80% of an initial capacity of 135 mAh g$^{-1}$ after 500 cycles. The reversible formation of Li$_2$O during cycling was confirmed by ex-situ NMR and XPS studies, while ex-situ NMR suggests that SiO$_2$ does not undergo redox activity during cycling. Therefore, the enhanced electrochemical performance may be ascribed to the enlarged interlayer spacing, which offers the dual benefit of increasing the available sites for Li intercalation and Li$_2$O formation, while significantly improving the structural stability during cycling. A potential parallel conversion reaction forming LiOH from -OH surface groups was implied by ex-situ $^1$H NMR and Raman results, but requires further detailed mechanistic studies to confirm the origin of any LiOH formed.
In a Na-ion system, the capacities of the non-pillared and pillared Mo$_2$TiC$_2$ MXene were up to a third lower than for the Li-ion system, which could be explained by the charge storage relying on Na$^+$ intercalation and capacitance, with no conversion reaction occurring. Nevertheless, the pillared material had superior performance compared to the non-pillared MXene, delivering reversible capacities up to 109 mAh g$^{-1}$ at 20 mA g$^{-1}$ over twice that of the non-pillared MXene.

**Experimental methods**

**Materials Synthesis and Pillaring**

For the synthesis of Mo$_2$TiAlC$_2$, Mo (-325 mesh, 98% purity, Sigma Aldrich), Ti (-325 mesh, 99% purity, Alfa Aesar), Al (-100+325 mesh, 99.5% purity, Alfa Aesar), and C (graphite, <20 µm, 99% purity, Sigma Aldrich) powders were mixed in a pestle and mortar in a 2:1:1.1:2 molar ratio. The mixture was then heated in a tube furnace under flowing argon at 1600 °C for 4 h, with a heating rate of 5 °C min$^{-1}$. The resulting block was then crushed with a pestle and mortar and ground to give a fine grey powder.

Typically, 3 g of Mo$_2$TiAlC$_2$ were slowly added to 30 ml of 9 M HCl with 3 g of pre-dissolved LiF. The mixture was heated to 60 °C and stirred for 5 days. The powder was recovered by centrifuging cycles, with DI water added after each cycle until the pH ≈ 6. The sample was then analysed by PXRD, which showed that significant amounts of unetched MAX phase remained in the sample. Therefore, the partially etched sample was re-dispersed in a fresh etching solution using the same volumes and concentrations used previously. After four days, the solid was collected via centrifuging, using the same protocol as described above. A washing step, where the powder was dispersed in 1 M HCl for 3 h at ambient temperature, was used to remove any salt impurities resulting from the etching step. A NaOH washing step was also attempted, but this caused the dissolution of the majority of the powder in approximately 30 min, showing that the Mo$_2$TiC$_2$ material is not stable in alkali conditions, in contrast to Ti$_3$C$_2$.

Interestingly, leaving the MAX phase to etch for nine consecutive days with no replenishing on the etching solution does not provide a well etched material, even when 12 M HCl is used with 6 g of LiF (the total amount used when the solution is replenished).

400 mg of the etched MXene was then added to a mixture of dodecylamine (DDA) dissolved in TEOS under argon (1:10:20 MXene:DDA:TEOS molar ratio). This was stirred in a glass vial sealed under argon at ambient temperature for 4 h. The product was then recovered by vacuum filtration and dried on filter paper under vacuum before being re-dispersed in DI water overnight at ambient temperature for 18 h. The intercalated hydrolysis product was then recovered by vacuum filtration and dried.
overnight at 60 °C, before calcination at 400 °C for 2 h with a heating rate of 5 °C min \(^{-1}\) under flowing argon to give the final pillared Mo\(_2\)TiC\(_2\).

**Material Characterisation**

**Powder X-ray diffraction (PXRD)** was carried out in a Smartlab diffractometer with a 9 kW rotating anode (Rigaku, Tokyo, Japan) using Cu Kα radiation (wavelength of 1.54051 Å) operating in reflection mode with Bragg-Brentano geometry. Prior to PXRD characterisation, all samples were dried in a heated oven at 80 °C for 18 h. The powders were then ground and placed on a silica sample holder and pressed flat with a glass slide.

**Scanning electron microscopy (SEM)** was performed in a JEOL JSM-7800F (JEOL, Tokyo, Japan), and energy-dispersive X-ray spectroscopy (EDS) was carried out using an X-Max50 (Oxford Instruments, Abingdon, UK) with an accelerating voltage of 10 kV and a working distance of 10 mm. The dried powder samples were dry cast onto a carbon tape support, which was placed on to a copper stub for analysis.

**Gas sorption isotherms** were measured on a Micromeritics 3 Flex 3500 gas sorption analyser using high purity nitrogen gas at 77 K. BET surface areas were calculated over a relative pressure range of 0.05-0.15 \(P/P_0\). Pore size distribution analysis was calculated using the NLDFT (non-linear density functional theory) method with a slit pore model using 3Flex Micromeritics software.

**Raman spectroscopy** was carried out on a Horiba Lab Raman Spectrometer (Horiba, Minami-ku Kyoto, Japan) with an EM-cooled Synapse camera. Spectra were collected using a 100x, 0.90 NA microscope objective. For each measurement, three scans were collected, with a total measurement time of 30 min. The dried powder was sandwiched between two glass microscope slides which were pressed together to give flat MXene particles. One of these slides was then discarded, with the other slide placed flat under the diode green laser (532 nm, 200 μW, 1% intensity) for measurements. For ex-situ measurements, the extracted discharged electrodes were washed with dimethyl carbonate (DMC), dried in the anti-chamber of an argon-filled glovebox, and transported to the spectrometer in a sealed container. The spectra were collected under air.

**Electrochemical characterisation**

Pillared and non-pillared Mo\(_2\)TiC\(_2\) were tested in coin cells (CR2032 type) in a half-cell configuration using lithium or sodium metal (Tob Energy, China) disks as the counter and reference electrodes and 1 M LiPF\(_6\) or NaPF\(_6\) in EC/DEC (1:1 weight ratio) as the electrolyte. The MXene (active material) was
mixed with carbon black (super P) as a conductive additive and PVDF as the binder in a 75:15:10 weight ratio respectively. The mixture was added to a few ml of NMP to make a slurry, which was then cast onto a Cu foil used as current collector, from which electrodes with a diameter of 16 mm were punched. The active mass loading of each electrode was ca. 3.2 mg cm$^{-2}$. Coin cells were constructed in an argon-filled glovebox (O$_2$ and H$_2$O levels < 0.1 ppm) using Whatman micro glass fibre paper as the separator. Galvanostatic tests were carried out on a Neware battery cycler (Neware Technology Ltd., China) at a current density of 20 mA g$^{-1}$ in the potential range of 0.01-3 V vs. Li$^+/\text{Li}$ for 94 cycles for the tests in the Li-ion half-cells and in the potential range of 0.01-3 V vs. Na$^+/\text{Na}$ for 80 cycles for the tests in the Na-ion half-cells. For rate capability tests, the cells were cycled at a current density of 20 mA g$^{-1}$ for 1 cycle to stabilise the cell before 5 cycles were run at each current density of 20, 50, 200, 500 and 1000 mA g$^{-1}$ before returning to 20 mA g$^{-1}$. For the long-term high-rate cycling test on the pillared MXene, 500 cycles were run at a rate of 1 A g$^{-1}$ after the rate capability test. Cyclic voltammetry (CV) measurements were conducted using an ivium potentiostat (Ivium Technologies BV, The Netherlands) with increasing scan rates of 0.2, 0.5, 2 and 5 mV s$^{-1}$ for 2 cycles at each rate in the potential range of 0.01-3 V vs. Li$^+/\text{Li}$ and Na$^+/\text{Na}$ for the tests in Li-ion and Na-ion half-cells, respectively. In each case the final cycle at each scan rate was used to calculate the b-values.

**Ex-situ X-ray photoelectron spectroscopy (XPS).** Electrodes were extracted from the cells at different states of charge (i.e. OCV, 0.01 V and 3 V). These were washed with dimethyl carbonate (DMC), dried under vacuum in the antechamber of an argon-filled glovebox and sealed under argon in a vial prior to measurement. Samples were analysed using a micro-focused monochromatic Al X-ray source (19.2 W) over an area of approximately 100 µm on a Thermo Fisher Scientific NEXSA spectrometer. Data were recorded at pass energies of 150 eV for survey scans and 40 eV for high-resolution scans with 1 eV and 0.1 eV step sizes respectively. Charge neutralisation of the sample was achieved using a combination of both low energy electrons and argon ions. To remove any surface contaminants, cluster cleaning was performed with 2 keV energy at 0.5x0.5 mm area for 60 s. Peak fitting and analysis was carried out using CASA-XPS software.

**Ex-situ Solid-state Nuclear Magnetic Resonance Spectroscopy (NMR).** $^{19}$F, $^7$Li, $^1$H and $^{29}$Si solid-state NMR spectra were obtained at 16.4 T on a Bruker Advance 700 MHz spectrometer (Bruker Biospin Corporation) operating at Larmor frequencies of 658.6, 272.1, 700.1 and 139.1 MHz, respectively. Spectra were referenced to PTFE (CF$_2$ = -122 ppm), alanine (NH$_3$ = 8.5 ppm) and kaolinite (-91.2 ppm) for $^{19}$F, $^1$H and $^{29}$Si, respectively. A 2D $^{19}$F-$^7$Li heteronuclear correlation spectrum was obtained using a cross-polarisation based sequence with the contact pulse ramped for $^{19}$F. This spectrum was used as an internal reference for the $^7$Li spectra, (LiF = -1 ppm). Powdered samples were packed, in a nitrogen filled glovebox, into 2.5 mm MAS rotors, and rotated at MAS rates of 15-30 kHz. Pellet electrodes
consisting of MXene powders, conductive carbon and PVDF binder in a 75:15:10 weight ratio were prepared by first mixing the components with a mortar and pestle and then adding small amounts of ethanol as the solvent. Around 25 mg of MXene powder were used in each pellet electrode. These electrodes were then cycled to different states-of-charge (i.e. discharged to 0.01 V and charged to 3 V) and then washed with DMC and dried under vacuum in the antechamber of a nitrogen filled glovebox. A pristine electrode was prepared to use as reference.

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Silica-Pillared Mo$_2$TiC$_2$ MXene for High-Power and Long-Life Lithium and Sodium-ion Batteries

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Table S1. Comparison of interlayer spacings and surface areas of previously published pillared MXenes and porous Mo-based MXene materials.................................................................................................................................Page 19

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Figure S1. EDS analysis of as-etched Mo$_2$TiC$_2$. a) EDS spectrum of area highlighted in b), which is the corresponding SEM image.
Figure S2. TGA plot showing the mass change of Mo$_2$TiC$_2$ against temperature. The thermal stability of Mo$_2$TiC$_2$ was investigated using TGA since this is directly relevant to the pillaring process, and has not been reported in the literature. Data were collected between 25 and 700 °C in air, with a heating rate of 1 °C min$^{-1}$. The mass changes very little up to around 350 °C, before increasing rapidly between 350-400 °C. This is followed by a period of more gradual mass increase between 400 and 600 °C with a very rapid increase between 600 and 700 °C. These results suggest that above 350 °C the MXene undergoes oxidation in a similar way to titanium based MXenes, likely resulting in the formation of Mo and Ti oxides. For the purpose of this study, the TGA results show that the material is unstable in temperatures exceeding 350 °C, so the calcination step used in the pillaring process (400 °C) was done under argon.
Raman modes can be observed at around 170, 240, 310, 450, 650 and 775 cm\(^{-1}\) in all samples, with no significant changes as a result of the pillaring process visible. These modes closely match previous reports on the Raman spectra of Mo\(_2\)TiC\(_2\), giving further evidence to the successful synthesis of Mo\(_2\)TiC\(_2\).\(^1\,^2\) It has been reported that the peak around 170 cm\(^{-1}\) results from the Eg vibration of both Mo and Ti atoms in –O terminated Mo\(_2\)TiC\(_2\).\(^2\) The Raman mode at around 240 cm\(^{-1}\) corresponds directly to the Eg vibration of the O atoms.\(^2\) This supports the EDS results, which suggested the presence of Mo-O in this MXene. The modes at 310, 450 and 650 and 750 cm\(^{-1}\) are all thought to mostly originate from the vibrations of C atoms in the MXene.\(^1,^2\) It should be noted that there are some differences in assignment in the literature, with Chen et al. assigning the 450 cm\(^{-1}\) peak to C vibrations, while Kim et al. assign it to -O surface vibrations.\(^1,^2\)

The intercalated pillared material shows additional Raman modes between 1000 and 1700 cm\(^{-1}\) which are much more intense than the MXene peaks. These broad peaks correspond to DDA vibrations, and match the modes seen in intercalated Ti\(_3\)C\(_2\) Raman spectra in our previous work, suggesting that DDA has been successfully intercalated. These modes are significantly reduced in the calcined material with only a small broad peak at 1600 cm\(^{-1}\) distinguishable, which shows that the majority of the carbon template has been removed after calcination, as was the case for the Ti\(_3\)C\(_2\) MXene. However, a small amount of graphitic carbon remains in the structure.

**Figure S3** Raman spectra of the non-pillared (Mo\(_2\)TiC\(_2\), red), pillared (Mo\(_2\)TiC\(_2\)-Si, green) and calcined (Mo\(_2\)TiC\(_2\)-Si-400, blue) MXene materials.
Figure S4. EDS spectrum of the calcined Mo$_2$TiC$_2$ flake.
Figure S5. Pore size distribution for the pillared Mo$_2$TiC$_2$-Si-400 material, calculated using the non-linear density functional theory (NLDFT) method with a slit pore model from N$_2$ adsorption experiments carried out at 77 K.
Figure S6. Ti 2p XPS spectra for a) non-pillared Mo$_2$TiC$_2$ and b) SiO$_2$-pillared Mo$_2$TiC$_2$ after calcination at 400 °C, Mo$_2$TiC$_2$-Si-400.
Figure S7. Differential capacity plots ($dQ/dV$) of selected cycles for non-pillared Mo$_2$TiC$_2$ cycled in the voltage range of 0.01-3 V vs. Li$^+/Li$ at a current density of 20 mA g$^{-1}$. a) Cycle 1, b) cycle 2, c) cycle 10, d) cycle 50 and e) cycle 94.
Figure S8. Differential capacity plots (dQ/dT) of selected cycles for SiO$_2$-pillared Mo$_2$TiC$_2$ cycled in the voltage range of 0.01-3 V vs. Li$^+$/Li at a current density of 20 mA g$^{-1}$. a) Cycle 1, b) cycle 2, c) cycle 10, d) cycle 50 and e) cycle 94.
Figure S9. Wide-spectrum view of ex-situ $^7\text{Li}$ NMR of the 0.01 V discharged Mo$_2$TiC$_2$-Si-400 pillared MXene. There is no peak in the between 20 and 10 ppm, where Li$_x$Si$_y$ alloys would be expected to form.$^3$
Figure S10. Ex-situ $^1$H MAS NMR spectra (16.4 T, 30 kHz MAS) of Mo$_2$TiC$_2$-Si-400. Assignments are based on previous reports.$^4$
Figure S11. Ex-situ Raman spectra on the discharged pillared MXene, Mo$_2$TiC$_2$Si-400. The pristine electrode is included for comparison. The grey area highlights the region where the vibrations correspond to the presence of Mo-O groups. The area with a white background shows the peaks which correspond to the main body of the MXene, M-M, M-X and X-X vibrations. A full description on the assignment of the MXene peaks can be found in Figure S3.
**Figure S12.** Ex-situ $^7$Li MAS NMR spectra (16.4 T, 30 kHz MAS) of Mo$_2$TiC$_2$-Si-400. Assignments were based on previous reports on $^7$Li NMR$^{5,6}$ and our $^{19}$F NMR results (Figure S13).
Figure S13. a) Ex-situ $^{19}$F MAS NMR spectra (16.4 T, 30 kHz MAS) of SiO$_2$-pillared Mo$_2$TiC$_2$. * indicate spinning sidebands. Assignments are based on previous reports for fluorine compounds.\textsuperscript{5} These are supported by: b) $^{19}$F-$^7$Li HETCOR spectrum (Lithium fluoride) and c) $^{19}$F MAS NMR spectrum of PVDF.
Figure S14. Cyclic voltammograms collected in the voltage range of 0.01-3 V vs. Li⁺/Li at a scan rate of 0.2 mV s⁻¹ for a) non-pillared Mo₂TiC₂ and b) pillared Mo₂TiC₂-Si-400.
Figure S15. Cyclic voltammograms collected in the voltage range of 0.01-3 V vs. Li+/Li at increasing scan rates of 0.2, 0.5, 2 and 5 mV s⁻¹ for a) non-pillared Mo₂TiC₂ and b) pillared Mo₂TiC₂-Si-400. Plots of b-value against voltage for c) non-pillared Mo₂TiC₂ and d) pillared Mo₂TiC₂-Si-400.
Figure S16. Differential capacity plots (dQ/dV) of selected cycles for non-pillared (top) and SiO₂-pillared (bottom) Mo₂TiC₂ cycled in a voltage range of 0.01-3 V vs. Na⁺/Na at a current density of 20 mA g⁻¹. a) Cycle 1 non-pillared Mo₂TiC₂. b) Cycle 2 non-pillared Mo₂TiC₂. c) Cycle 1 pillared Mo₂TiC₂. d) Cycle 2 pillared Mo₂TiC₂.
Figure S17. Cyclic voltammograms collected in the voltage range of 0.01-3 V vs. Na⁺/Na at increasing scan rates of 0.2, 0.5, 2 and 5 mV s⁻¹ for a) non-pillared Mo₂TiC₂ and b) pillared Mo₂TiC₂-Si-400. Plots of 𝑏-values against voltage vs. Na⁺/Na. for c) non-pillared Mo₂TiC₂ and d) pillared-Mo₂TiC₂.
| Material | Interlayer spacing (nm) | BET Surface area (m² g⁻¹) | Reference |
|----------|-------------------------|----------------------------|-----------|
| CTAB and Sn⁺⁺ Pillared Ti₃C₂ | 1.47-2.7 | N/a | 7 |
| Li, Na, K Pillared Ti₃C₂ | 1.26 | N/A | 8 |
| CTAB and Sn⁺⁺ Pillared Ti₃C₂ | 1.9-2.2 | N/A | 9 |
| TAEA Pillared Ti₃C₂ | 1.38 | N/A | 10 |
| Pyrolised Amine Pillared Ti₃C₂ | 0.99-2.83 | 9 | 10 |
| Ti₃C₂-CNT | 1.64 | 117 | 11 |
| SiO₂ Pillared Ti₃C₂ | 1.49-4.24 | 235 | 12 |
| Mo₂C-CNT “thin film paper” | 1.9 | N/A | 13 |
| Mo₂C-TBAOH | 2.9 | N/A | 13 |
| Mesoporous Mo₂C (UV etched) | 1.75 | N/A | 14 |
| TiO₂ Pillared MoS₂ | 1.65 | 186 (Langmuir Surface area) | 15 |
| MoO₃(OH)ₓ Pillared MoS₂ | 0.63 | 81 | 14 |
| Mo₂TiC₂ (HF etched) | 1.3 | N/A | 16 |
| Delaminated Mo₂TiC₂ (HF etched) | 2.1 | N/A | 2 |
| Mo₂TiC₂ (LiF etched) | 1.2 | 8 | This Work |
| SiO₂ Pillared Mo₂TiC₂ (LiF etched) | 2-4 | 202 | This Work |
Table S2. Comparison of the electrochemical performance of various Mo-based MXenes as negative electrodes in lithium-ion batteries, showing the superior performance of the SiO$_2$ pillared Mo$_2$TiC$_2$.

| Material                                | Initial Capacity (mAh g$^{-1}$) | 2$^{nd}$ Cycle Capacity (mAh g$^{-1}$) | Initial Coulombic Efficiency (%) | Capacity retention (%) | High Rate Capacity (mAh g$^{-1}$) | Ref. |
|-----------------------------------------|---------------------------------|----------------------------------------|----------------------------------|------------------------|-----------------------------------|------|
| Mo$_2$C-CNT “thin film paper” (HF etched) | 821 (10 mA g$^{-1}$)            | 423 (10 mA g$^{-1}$)                   | 76%                             | 132% (400 mA g$^{-1}$, 70 cycles) | ~180 (5 A g$^{-1}$, ~138%, 1000 cycles) | 13   |
| Mesoporous Mo$_2$C (UV etched)          | ~280 (5 mA g$^{-1}$)            | ~170 (5 mA g$^{-1}$)                   | ~60%                            | ~53% (5 mA g$^{-1}$, 140 cycles) | 45 (1 A g$^{-1}$) | 14   |
| Mo$_2$TiC$_2$ (HF etched)               | 311 (0.1 C)                     | ~260 (0.1 C)                           | 86%                             | 92% (0.1 C, 25 cycles) | 144 (1 C 82%, 160 cycles) | 16   |
| Delaminated Mo$_2$TiC$_2$ (HF etched)   | 268 (100 mA g$^{-1}$)           | 134 (100 mA g$^{-1}$)                  | 50%                             | 39% (100 mA g$^{-1}$, 100 cycles) | ~0 (1 A g$^{-1}$) | 2    |
| Mo$_2$TiC$_2$ (LiF etched)              | 344 (20 mA g$^{-1}$)            | 219 (20 mA g$^{-1}$)                   | 64%                             | 54% (20 mA g$^{-1}$, 94 cycles) | 59 (1 A g$^{-1}$) | This Work |
| SiO$_2$ Pillared Mo$_2$TiC$_2$ (LiF etched) | 473 (20 mA g$^{-1}$)           | 316 (20 mA g$^{-1}$)                   | 66%                             | 80% (20 mA g$^{-1}$, 100 cycles) | 143 (1 A g$^{-1}$, 80%, 500 cycles) | This Work |

This Work
Table S3. Comparison of the electrochemical performance of various non Ti-based MXenes as negative electrodes in sodium-ion batteries.

| Material                                      | Initial Capacity (mAh g$^{-1}$) | 2nd Cycle Capacity (mAh g$^{-1}$) | Initial Coulombic Efficiency (%) | Capacity retention (%) | High Rate Capacity (mAh g$^{-1}$) | Ref.     |
|-----------------------------------------------|----------------------------------|-----------------------------------|----------------------------------|------------------------|-----------------------------------|---------|
| Mesoporous Mo$_2$C (UV etched)                | 320 (5 mA g$^{-1}$)              | ~70 (5 mA g$^{-1}$)               | 15%                              | ~70%                   | ~15 (1 A g$^{-1}$)                | 14      |
| Mo$_2$Ti$_2$C$_2$ (LiF etched)                | 151 (20 mA g$^{-1}$)             | 74 (20 mA g$^{-1}$)               | 41%                              | 65%                    | 18 (1 A g$^{-1}$)                 | This Work |
| SiO$_2$ Pillared Mo$_2$Ti$_2$C$_2$ (LiF etched)| 205 (20 mA g$^{-1}$)             | 109 (20 mA g$^{-1}$)              | 49%                              | 75%                    | 40 (1 A g$^{-1}$)                 | This Work |
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