

Article

Influence of MXene/MXene-Oxide Heterostructure Chemistry and Structure on Lithium-Ion Battery Anodes and Supercapacitor Electrodes

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Abstract

The global decarbonisation strategy has accelerated the shift toward renewable energy and electric transport, demanding advanced electrochemical energy storage systems. Conventional anodes such as graphite and silicon composites face challenges in conductivity, stability and cycling performance. MXenes, a class of two-dimensional (2D) materials, offer promising alternatives owing to their metallic conductivity, tunable surface chemistry and high theoretical capacity. Here, we synthesise and characterise $\text{Mo}_2\text{TiC}_2\text{T}_x$ and V_2CT_x ($T = \text{O}, \text{OH}, \text{F}$ and/or Cl) MXenes for lithium-ion battery anodes and supercapacitors. Unlike $\text{Ti}_3\text{C}_2\text{T}_x$, which stores charge via intercalation and surface redox reactions, $\text{Mo}_2\text{TiC}_2\text{T}_x$ and V_2CT_x exhibit conversion-type mechanisms. We also identify novel $\text{V}_2\text{C}-\text{VO}_x$ heterostructures, achieving a specific capacitance of 532.4 F g^{-1} at 2 mV s^{-1} and an initial capacity of 493.3 mAh g^{-1} at 50 mA g^{-1} in lithium half-cells, with a low decay rate of 0.071% per cycle over 200 cycles. Pristine $\text{Mo}_2\text{TiC}_2\text{T}_x$ shows 391.7 mAh g^{-1} at 50 mA g^{-1} , decaying by 0.109% per cycle. These results experimentally validate theoretical predictions, revealing how MXene structure and transition metal chemistry govern electrochemical behaviour, thus guiding electrode design for next-generation batteries and supercapacitors.

Keywords: MXene; lithium-ion; batteries; supercapacitors; $\text{Mo}_2\text{TiC}_2\text{T}_x$; V_2CT_x scrolls; MXene-oxide heterostructure



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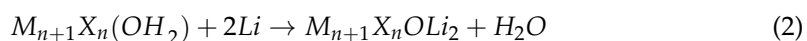
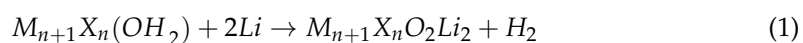
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1. Introduction

Lithium-ion batteries (LIBs) are an integral part of the global decarbonisation strategy. With this growing demand comes a technological race to develop novel advanced material chemistries to obtain an edge in enhancing battery performance. One of the large domains of research focus is the anodes which are typically associated with enhancements in energy capacity, charging times and cycling durability (capacity retention). Moving on from conventional graphitic and hard carbon anodes, materials such as silicon, silicon oxide and silicon carbides have become a stepping stone and core area of commercialisation that will eventually segue to solid-state (and metallic anode) batteries [1,2]. However, although these materials improve the capacity of the devices, they primarily suffer from poor conductivities and rapid degradation. Various strategies have been employed to improve the performance of such materials by reducing particle size, alloying the element and finding a common route of nanoparticle encapsulation within a host matrix [2,3].

Graphene (and derivatives), such as those that are commercially viable at the required volume, namely reduced graphene oxide and liquid-phase exfoliated graphite (forming graphene nanoplatelets, also referred to as GNP) are widely researched host matrix materials for silicon. However, they still suffer from poor conductivity due to intrinsic defects and structural compositions arising from the chosen manufacturing routes. Therefore, this is an area in which alternative host materials such as MXenes are being widely researched; unlike GNP, MXenes are intrinsically conductive regardless of their few-layer structures, and they do not suffer from in-plane defects typical in reduced graphene oxide, as MXene synthesis avoids the significant structural changes that reduce conductivity in graphene-based matrices.

MXenes are intrinsically metallic with surface moieties that not only make them processible in polar and non-polar solvents (a benefit for commercial manufacturing) but also contribute to surface based pseudo-capacitive reactions together with electrochemical double-layer capacitance (EDLC). This has the potential to not only improve the conductivity of the anode, which could lead to more efficient batteries with faster charging times but also, consequentially, greater energy capacities with enhanced durability. MXenes have demonstrated significant enhancements to various aspects of electrochemical energy storage [4]. However, with regard to their application as anode materials in LIBs, the charge storage mechanism falls into two main types, which are intercalation (structure-dependent) and conversion via surface-mediated reactions. One of the first studies on MXenes for anodes in LIBs was a work by M. Naguib et al. [5]. In this work, they accomplished Li insertion into layered, partially oxidised Ti_2C fabricated using the HF process. The peak capacity they were able to obtain was 225 mA h g^{-1} at 0.04 C . At 10 C , it managed to retain 70 mA h g^{-1} after 200 cycles. These early experimental discoveries demonstrated the capability of MXenes as Li anode materials and subsequently led to a flurry of research activity, both theoretical and experimental, in this area [6].

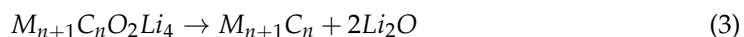


In 2014, Y. Xie et al. [7] performed early experimentation and density functional theory (DFT) simulations to evaluate how the surface structure of MXenes impacted the Li-ion energy storage capacity. The discoveries made were extensive, hence their findings will be briefly summarised here. Firstly, they established that the nature of the surface functional groups played a big role in the theoretical capacity of the MXene and thus also found that, generally, -O terminations on the MXenes exhibit the highest theoretical Li-ion storage capacity. In their experimental work, they found that Ti_2C , V_2C , Nb_2C and Ti_3C_2 had vastly superior lithium capacities than what was theoretically predicted [8]. This therefore called for a new description to explain where the excess capacity was coming from. They established through DFT simulations that it was energetically favourable for additional Li atoms to adsorb onto lithiated -OH passivated surfaces and thus was unfavourable for Li intercalation [7]. However, surface reaction of -OH with Li could result in conversion of -OH into -O terminations or bare MXene (Equations (1) and (2)), which was favourable as it enabled an increased number of adsorbed Li^+ ions on the MXene surface. However, they found that this was still insufficient to explain the increased capacity. This additional capacity could be further explained by the ability of additional Li layers to form atop the lithiated O-terminated MXenes [7]. This was also supported by the fact that delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ had significantly higher Li storage capacity than the conventionally stacked $\text{Ti}_3\text{C}_2\text{T}_x$ found from HF etching. A further interesting observation that these authors made was that Nb_2C and V_2C MXenes had experimentally higher reversible Li capacities compared to Ti-

containing MXenes, potentially due to inherently fewer -OH groups (lower concentration) resulting in faster Li diffusion and fewer trapped reaction products [7]. Additionally, the low diffusion barriers of O-terminated MXenes enabled facile Li-ion movement, thus allowing the MXenes to perform at high rates.

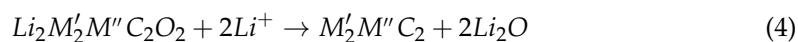
The authors subsequently also built upon their work and studied the applications of MXenes in non-lithium-ion batteries. Similarly, they found that O-terminated (and bare) MXenes had excellent characteristics for implementation as anode materials [9]. In addition, the charge storage processes experienced by MXenes are more complex than originally thought. Initially, as found previously, the -OH will convert into an -O termination, which can then form metal oxides (with the inserting ion) and bare MXenes via a reversible conversion reaction (as seen in Equation (3)). Furthermore, metal ions can further intercalate into the bare MXene, forming a metallic surface adsorbed layer (more than one layer will form in the case of Mg^{2+} and Al^{3+}) [9]. Hence, MXenes can experience three storage mechanisms cumulatively, which are conversion reactions, intercalation/deintercalation and plating/stripping (of the metal deposited on the MXene surface). Further theoretical studies have validated the discoveries and observations made by these authors [10,11].

Considering these theoretical discoveries, we can observe in experimental work by R. Cheng et al. [12] that modifications to $Ti_3C_2T_x$ surface structures can significantly affect Li-ion storage behaviour. NH_3 treatment of $Ti_3C_2T_x$ results in one redox couple as opposed to the expected double-redox couple in as-synthesised $Ti_3C_2T_x$. This is attributed to variations in the interlayer spacing, which affects Li diffusion. Hence, physical characteristics such as MXene sheet size and interlayer spacing also have governance of the overall performance of MXene in the anode, bridging theoretical understanding and what can be achieved in practice. Studies by H. Zhang et al. [13] experimentally validated that, by carefully annealing $Ti_3C_2T_x$, they were able to successfully reduce the amount of -F and -OH terminations on the MXene, which not only enhanced the electronic conductivity of the material but was also able to enhance the adsorption of Li, resulting in greater charge storage capabilities of 221 mA h g^{-1} at 0.1 C (where C was defined as 320 mA h g^{-1}).



Moving away from $Ti_3C_2T_x$, B. Yan et al. [14] explored how the surface chemistry of V_2CT_2 (whereby T was -O or -S) could influence the performance of the MXene. Computational results demonstrated that -F and -OH on V_2C inhibited rapid Li-ion transport, thus reducing the lithium capacity of the material significantly. However, if -O and -S terminations were anchored to V_2C , the material remains metallic, even after lithiation, whilst lithiated -F and -OH sites were semi-metallic (low band gap semiconductors). Subsequent experimental studies by F. Liu et al. [15] supported these discoveries and managed to observe a capacity of 260 mA h g^{-1} at 370 mA g^{-1} with high purity V_2CT_x . Further to this, Anasori et al. [16] carried out a blended computational and experimental study comparing the performance of Mo-based MXenes— Mo_2TiC_2 , $Mo_2Ti_2C_3$ and Ti_3C_2 —as electrodes for lithium-ion batteries and supercapacitor electrodes. An insightful take away from this study was that, despite $Mo_2TiC_2T_x$ and $Ti_3C_2T_x$ being isostructural (only surface metal atoms differ), their electrochemical behaviour differs, suggesting that Ti atoms do not play a major role in the electrochemical behaviour of the molybdenum MXene, i.e., the material behaves as a pure Mo MXene. Beyond demonstrating the analogues of lithium adsorption energy of a Mo_2TiC_2 MXene to a theoretical Mo_3C_2 MXene, the authors demonstrated the electrochemical behaviour of Mo_2TiC_2 as lithium-ion battery and supercapacitor electrodes. As a lithium-ion battery electrode, the MXene exhibited good Coulombic efficiency >90% at 180 cycles. A $12\text{ }\mu\text{m}$ MXene ‘paper’ electrode demonstrated a good capacitance of 342 F cm^{-3} at 2 mV s^{-1} and 167 F cm^{-3} at 10 mV s^{-1} . Galvanostatic cycling also demon-

strates excellent capacitance retention at 10,000 cycles. Additionally, the majority of the lithiation for $\text{Mo}_2\text{TiC}_2\text{T}_x$ occurs below 0.6 V vs. Li/Li^+ . This is indicative of the conversion reaction in Equation (3), albeit slightly altered, as can be seen in Equation (4). Notably, however, this conversion reaction was found to not be energetically favourable for the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, which will only undergo the $-\text{OH}$ to $-\text{O}$ conversion upon Li^+ adsorption.



Another interesting approach was investigated by P.A. Maughan et al. [17]. In one of the only studies with $\text{Mo}_2\text{TiC}_2\text{T}_x$, the authors, for the first time, utilised a 9-day MILD etching method to synthesise multilayered $\text{Mo}_2\text{TiC}_2\text{T}_x$. Following this, they intercalated the layered structure with tetraethyl orthosilicate which, after hydrolysis and calcination, turned into SiO_2 pillared Mo_2TiC_2 . This novel approach (considering the MXene composition being studied) resulted in a specific capacity of 320 mA h g^{-1} at 1 A g^{-1} , with 80% retained after 500 cycles. This study is promising, as it indicates that if Si-based composites can be integrated into delaminated $\text{Mo}_2\text{TiC}_2\text{T}_x$, there could potentially be even greater synergistic effects than $\text{Ti}_3\text{C}_2\text{T}_x$. This is because Mo-based MXenes would naturally have a higher concentration of $-\text{O}$ terminations on the surface (if synthesised with the HF method), allowing for more conversion reactions to occur, which will add to the already high capacity of Si. This therefore warrants further investigation.

Lastly, an aspect that should be considered is that the compositing of MXenes to form anode materials for LIBs is not limited to Si. Work by Z. Zhang et al. [18] demonstrated that Fe_2O_3 nanoparticles, which are a conversion reaction material, could be deposited onto crumpled Ti_3C_2 , creating an electrode with enhanced electrochemical performance. They observed a high reversible capacity of 1065 mA h g^{-1} at 100 mA g^{-1} with 549 mA h g^{-1} retained after 400 cycles at 2 A g^{-1} . This promising performance demonstrates the versatility of MXenes to behave as a host material to enhance various characteristics of other promising anode materials. An abundance of work has further explored the integration of MXene composites for LIB anodes, employing various strategies to attempt to address the challenges faced by Si anodes. Some of these strategies might include encapsulation of Si nanoparticles in porous nanospheres of $\text{Ti}_3\text{C}_2\text{T}_x$ [19], anchoring of SiO_2 on laminated $\text{Ti}_3\text{C}_2\text{T}_x$ [20] or even self-assembling of 3D porous structures with MXene-wrapped Si nanoparticles [21]. We should also note that MXene has also been applied in areas beyond anode formulations. The literature has demonstrated the capability of MXenes to have functional enhancements to the separator [22], as electrolyte additives or anode modifications in solid-state cells [23–28], freestanding current collectors [29,30], interfacial modifiers [31–39] and conductive additives [40]. Cumulatively, previous works have provided evidence that MXene has the potential for synergistic effects when composited, highlighting its capability in creating more capable anode compositions and designs for future battery systems.

Overall, previous collective works demonstrate the unique and complex nature in which MXenes behave as anodic materials in LIBs. They experience a multi-faceted charge storage mechanism, which makes them stand out in the larger area of battery anode development. For the first time, this work carries out direct experimental comparative studies that explore how three different as-synthesised high purity few-layer MXenes of various transition metal chemistry ($\text{Ti}_3\text{C}_2\text{T}_x$, $\text{Mo}_2\text{TiC}_2\text{T}_x$ and V_2CT_x) and structure (multi-layer $\text{Ti}_3\text{C}_2\text{T}_x$ —ML- $\text{Ti}_3\text{C}_2\text{T}_x$) behave in lithium-ion half-cells, investigating their behaviour as host-matrix materials for future battery anodes. In addition to this, the investigation is extended to evaluate their capacitive performance for pseudo-capacitive or asymmetric supercapacitor electrodes.

In this work, we present an extensive experimental investigation into the synthesis, structural characterisation and electrochemical evaluation of MXenes with differing transi-

tion metal chemistries and structures, namely $\text{Ti}_3\text{C}_2\text{T}_x$, multi-layer $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{Mo}_2\text{TiC}_2\text{T}_x$ and V_2CT_x . The study aims to elucidate how variations in surface terminations, morphology and elemental composition influence their charge storage behaviour in lithium-ion batteries and supercapacitors. Through systematic comparison, this work establishes the relationship between MXene chemistry, structural configuration and electrochemical performance, offering fundamental insights to guide the rational design of next-generation MXene-based electrodes for high-performance energy storage applications.

2. Materials and Methods

2.1. $\text{Ti}_3\text{C}_2\text{T}_x$ MXene Synthesis

$\text{Ti}_3\text{C}_2\text{T}_x$ was synthesised using a variation of the minimally invasive layer delamination (MILD) method. In an HDPE vessel, 3 M of LiF was dissolved in 9 M HCl under stirring, and 3 g of Ti_3AlC_2 MAX phase was added. The mixture was stirred at 60 °C for 24 h, then cooled and diluted with deionized water (DIW) before centrifugation at 3500 RPM. The sediment was re-dispersed in DIW and centrifuged repeatedly until the supernatant became translucent. The supernatant was concentrated by centrifugation at 11,000 RPM, and the sediment was freeze-dried.

2.2. $\text{Mo}_2\text{TiC}_2\text{T}_x$ MXene Synthesis

$\text{Mo}_2\text{TiC}_2\text{T}_x$ was synthesised using a two-step HF etching and delamination process. A total of 2 g of $\text{Mo}_2\text{TiC}_2\text{T}_x$ was added to 20 mL of 48% HF and stirred at 55 °C for 72 h. After cooling, the mixture was washed by centrifugation at 11,000 RPM until the supernatant reached pH 6. The sediment was dispersed in 1 wt% TBAOH, vortex-mixed and sonicated for 2 h. The product was centrifuged, washed with DIW and freeze-dried. Only the few-layer $\text{Mo}_2\text{TiC}_2\text{T}_x$ was used for experimentation.

2.3. Multi-Layer $\text{Ti}_3\text{C}_2\text{T}_x$ (ML- $\text{Ti}_3\text{C}_2\text{T}_x$) MXene Synthesis

Multi-layer $\text{Ti}_3\text{C}_2\text{T}_x$ was synthesised by slowly adding 2 g of Ti_3AlC_2 to 20 mL of 48% HF and stirring for 2 h. The mixture was centrifuged at 3500 RPM and washed with DIW until the supernatant reached pH 6. The sediment was freeze-dried.

2.4. V_2CT_x (Scrolls) MXene Synthesis

V_2CT_x was synthesised using an in situ etching method. A total of 1 g of V_2AlC was dispersed in 40 mL of 9 M HCl and 3.2 g of LiF and stirred at 60 °C for 120 h. After washing to pH 6, the product was sonicated in 1 M TMAOH for 2–3 h, then washed until the supernatant reached pH 7. The supernatant was freeze-dried.

2.5. Electrode and Cell Fabrication

The electrode slurries were prepared by hand-grinding the freeze-dried powdered MXene ($\text{Ti}_3\text{C}_2\text{T}_x$, $\text{Mo}_2\text{TiC}_2\text{T}_x$, ML- $\text{Ti}_3\text{C}_2\text{T}_x$ and V_2CT_x), carbon black (Super P[®]), styrene butadiene rubber (SBR) and carboxymethyl cellulose (CMC) with a mass ratio of 90:5:3:2 in deionized water until a homogeneous slurry was obtained. The slurry was then cast onto a copper foil with a doctor blade set at 100 µm. The coated foil was then dried in a vacuum oven at 60 °C for 24 h (under vacuum) before cutting into 15 mm electrode discs. The electrode discs were then transferred into an argon-filled glovebox ($\text{O}_2 < 0.1$ ppm, $\text{H}_2\text{O} < 0.1$ ppm) and assembled into CR2032 coin cells. A lithium chip was used as the counter electrode, together with a Celgard 2400 separator and 100 µL (in excess) of 1 M LiPF_6 in EC/DMC = 1:1 (v/v) (50 µL deposited on the electrode disc and another 50 µL deposited on the separator). The mass loading of the active materials was typically in the range of 1.1–6.0 mg cm^{−2}, corresponding to approximately 1.1 mg cm^{−2} for $\text{Ti}_3\text{C}_2\text{T}_x$,

1.5 mg cm^{-2} for V_2CT_x , 1.9 mg cm^{-2} for $\text{Mo}_2\text{TiC}_2\text{T}_x$ and 6.0 mg cm^{-2} for $\text{ML-Ti}_3\text{C}_2\text{T}_x$ electrodes. The cells were then left for 24 h before any testing was conducted. With regard to cell testing protocol, cells were first subjected to cyclic voltammetry, then to galvanostatic rate testing, followed by extended galvanostatic cycling. Unfortunately, electrochemical impedance spectroscopy of the cell could not be conducted in the duration of this work due to a lack of available channels.

3. Results

3.1. Synthesis and Characterisation of MXenes

$\text{Mo}_2\text{TiC}_2\text{T}_x$ was synthesised successfully from its MAX phase precursor $\text{Mo}_2\text{TiAlC}_2$ (Figure 1A) using the HF etching method. This method was also applied to synthesise the $\text{ML-Ti}_3\text{C}_2$ (Figure 1F) from the MAX phase Ti_3AlC_2 . The MILD method was used to synthesise V_2CT_x and $\text{Ti}_3\text{C}_2\text{T}_x$ from MAX phase precursors V_2AlC (Figure 1B) and Ti_3AlC_2 (Figure 1C), respectively. The synthesis methods used resulted in MXenes of various morphologies. In Figure 1D, we observe a clustered agglomeration of stacked $\text{Mo}_2\text{TiC}_2\text{T}_x$ MXene sheets. Although not as evident in this micrograph, the lateral dimensions of the MXene sheet are sub-micron, making it difficult to image via SEM. However, the absence of particulate materials and observed sheet-like morphologies indicate a somewhat successful etching and exfoliation of the $\text{Mo}_2\text{TiC}_2\text{T}_x$ MXene.

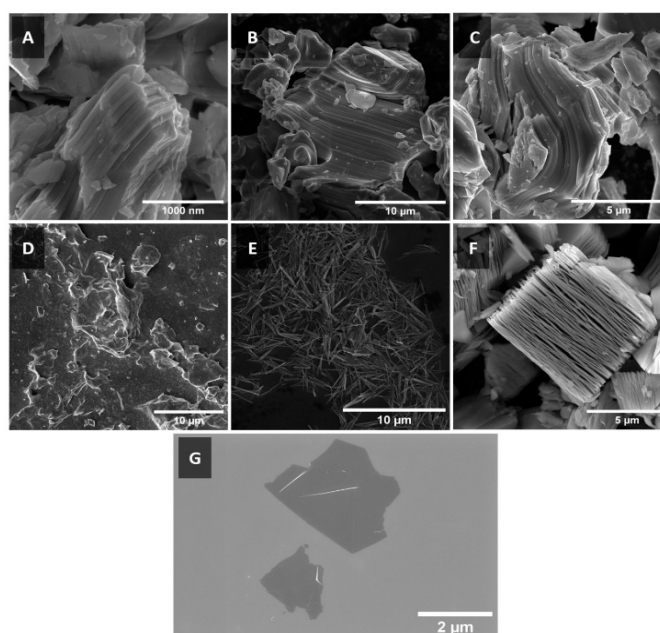


Figure 1. SEM micrographs of (A) $\text{Mo}_2\text{TiAlC}_2$, (B) V_2AlC , (C) Ti_3AlC_2 MAX phases and (D) $\text{Mo}_2\text{TiC}_2\text{T}_x$, (E) V_2CT_x , (F) multi-layer $\text{Ti}_3\text{C}_2\text{T}_x$ ($\text{ML-Ti}_3\text{C}_2\text{T}_x$), (G) $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes.

In Figure 1E, we can observe that the resulting V_2CT_x has formed needle-like scrolls instead of the expected 2D sheet morphology of MXenes. This is a unique outcome that has not been previously observed in the as-synthesised product of this MXene. It suggests that somewhere within the synthesis process, to minimise surface energy, the MXene sheet rolled up into itself, forming the scrolled morphology. A potential stage at which this may have occurred is the intercalation–exfoliation step in which TMAOH was used to intercalate the etched V_2AlC and then sonication was used to exfoliate V_2CT_x . Further work should be conducted to evaluate the exact nature of the scrolling effect, clarifying the exact mechanism of formation, which could lead to the development of targeted processes to create other scrolled MXenes.

In Figure 1F, we observe the ‘accordion-like’ structure of ML- $\text{Ti}_3\text{C}_2\text{T}_x$ formed by the HF etching process. This MXene morphology is formed by the etching of Al from Ti_3AlC_2 , coupled with the formation of a hydrogen gas by-product, causes expansion in the ‘c’ direction of the lattice, resulting in the observed accordion morphology. The steps in this synthesis process do not produce sufficient energy (or shear force) to induce the delamination of the individual $\text{Ti}_3\text{C}_2\text{T}_x$ sheets. In contrast, the use of a lithium salt in the MILD method results in intercalation of Li^+ ions in this expanded structure such that, when coupled with the centrifugation and shaking steps, it facilitates the exfoliation of 2D $\text{Ti}_3\text{C}_2\text{T}_x$ sheets, as can be seen in Figure 1G.

TEM of the as-synthesised MXenes also reflect a successful synthesis. In Figure 2A,B, we observe single- and few-layer sheets of $\text{Mo}_2\text{TiC}_2\text{T}_x$ and $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes. SAED on selected regions of the sheets demonstrates monocrystalline diffraction patterns on the set of planes (0 1 0), (1 0 0) and (1 -1 0) for $\text{Mo}_2\text{TiC}_2\text{T}_x$ (highest intensity diffraction spots in Figure 2D) and (−1 2 0), (1 1 0) and (2 -1 0) for $\text{Ti}_3\text{C}_2\text{T}_x$ (highest intensity diffraction spots in Figure 2E). This indicates the successful synthesis of single- and few-layer $\text{Mo}_2\text{TiC}_2\text{T}_x$ and $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes. TEM of V_2CT_x , as seen in Figure 2C, demonstrates an agglomerate of V_2CT_x MXene scrolls. SAED of a single scroll region results in a diffraction pattern in which the set of planes (0 1 0), (1 0 0) and (1 -1 0) are offset by a fixed vector angle (Figure 2F). However, the presence of a discrete electron diffraction pattern suggests that the scrolls are formed by single-layer V_2CT_x sheets, which is a novel discovery.

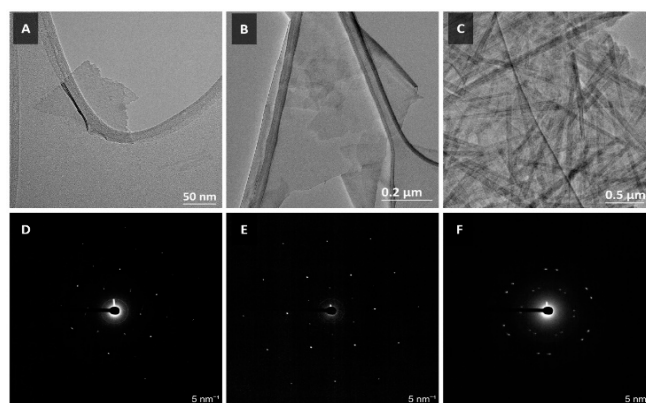


Figure 2. TEM micrographs of (A) $\text{Mo}_2\text{TiC}_2\text{T}_x$, (B) $\text{Ti}_3\text{C}_2\text{T}_x$ and (C) V_2CT_x MXenes. Images (D–F) are selected area electron diffraction (SAED) patterns of (A–C), respectively.

HRTEM analysis of the as-synthesised MXenes can be seen in Figure S1. A representative selection of the HRTEM micrographs (i) that outlines a highly magnified area of the MXene is de-noised and cleaned by passing the fast-Fourier transform (ii) of the selected region through a filter, resulting in a low-noise image (iii) which allows for more accurate measurements of lattice parameters from the observed fringes. The lattice parameters of $\text{Mo}_2\text{TiC}_2\text{T}_x$ as measured from Figure S3B are 2.98 Å in the (0 1 -1 0) and (1 0 -1 0) directions and 2.97 Å in the (1 -1 0 0) direction. These numbers are consistent with theoretical predictions [41]. For $\text{Ti}_3\text{C}_2\text{T}_x$, the measured lattice parameters were 2.58 Å in the (1 -1 0 0) and (1 0 -1 0) directions and 2.56 Å in the (0 1 -1 0), which are also consistent with theoretical predictions [42]. The slight variation in lattice spacing for both the MXenes across the basal planes might be attributed to some residual uncorrected objective astigmatism or errors in measurement. Unfortunately, the scrolled nature of the V_2CT_x MXene makes it difficult to resolve layer-specific lattice fringes (as seen in Figure S1C), hence the lattice spacing could not be determined from HRTEM.

To determine the elemental distribution of the respective MXenes, HAADF-STEM-EDS was conducted and can be observed in Figure S2. The bright spot observed on

$\text{Mo}_2\text{TiC}_2\text{T}_x$ in Figure S2A could be due to beam damage, which is further supported by the observed increase in carbon content in the local area in Figure S2A(iii). This supplementary characterisation method allows us to observe the homogeneous distribution of transition metals and surface atoms (oxygen, fluorine and chlorine) in the MXene. Quantitatively, it was found that for $\text{Mo}_2\text{TiC}_2\text{T}_x$, the atomic ratio of Mo to Ti was 2:1, consistent with the stoichiometric ratio. With respect to surface atoms on the MXene, the Mo to O ratio was found to be 1:2, while the Mo to F ratio was 1:0.7, i.e., the amount of oxygen moieties was roughly three times higher than fluorine. However, in $\text{Ti}_3\text{C}_2\text{T}_x$, the Ti to O atomic ratio was 1:1.7, with the Ti:F ratio being 1:0.3 and Ti:Cl ratio 1:0.1. V_2CT_x had a similar atomic ratio with V:O being roughly 1:1, V:F being 1:0.3 and V:Cl being 1:0.1. The difference between the two latter MXenes and $\text{Mo}_2\text{TiC}_2\text{T}_x$ is the presence of a small amount of chlorine, which can be attributed to the use of HCl as the etching reagent in the synthesis process. However, we also observe that there is a greater abundance of fluorine for the $\text{Mo}_2\text{TiC}_2\text{T}_x$ due to the use of HF and increased amounts of oxygen, potentially indicating partial oxidation. We conducted XPS, which further clarifies these results.

To further verify the successful synthesis of the MXenes, XRD was performed on freeze-dried powdered samples that were pressed into films. These resulting diffractograms of the MXenes and their MAX phase precursors can be observed in Figure S3. For all the MXenes synthesised, we observe the disappearance of diffraction peaks associated with basal planes in their MAX phase precursors, with the exception of the ML- $\text{Ti}_3\text{C}_2\text{T}_x$, where we can see a few very low intensity and broad peaks in the 35° to 45° 2θ region and a left shift with broadening of the (1 1 0) peak. This can be attributed to the fact that, although the MXene has been successfully etched, it has not been exfoliated, i.e., there is still some long-range crystallographic order, although the plane spacing has expanded, leading to the observed shift and broadening of the peaks. The shift to a lower angle and broadening of (0 0 2) peak indicate successful exfoliation. The determined (0 0 2) plane spacing was determined to be 1.25 nm for $\text{Mo}_2\text{TiC}_2\text{T}_x$, 1.32 nm for $\text{Ti}_3\text{C}_2\text{T}_x$, 1.21 nm for V_2CT_x and 1.00 nm for ML- $\text{Ti}_3\text{C}_2\text{T}_x$. These results alone indicate that the most successful exfoliation based on magnitude of the (0 0 2) spacing was $\text{Ti}_3\text{C}_2\text{T}_x$. However, it is known that $\text{Mo}_2\text{TiC}_2\text{T}_x$ and V_2CT_x have some of the highest exfoliation energies amongst MXenes [43]. Thus, although the (0 0 2) spacing for $\text{Ti}_3\text{C}_2\text{T}_x$ was larger, an important consideration is that greater inter-layer (or sheet) interactions in $\text{Mo}_2\text{TiC}_2\text{T}_x$ and V_2CT_x can lead to denser re-stacking and hence smaller (0 0 2) spacing. This can be observed experimentally, in that the freeze-dried exfoliated $\text{Mo}_2\text{TiC}_2\text{T}_x$ and V_2CT_x were significantly harder to disperse homogeneously in de-ionised water (DIW), requiring grinding and shear with a mortar and pestle to remove large clusters of agglomerated MXenes. Contrastingly, $\text{Ti}_3\text{C}_2\text{T}_x$ dispersed homogeneously upon addition of DIW with minimal stirring.

To determine the chemical composition of the MXenes, especially to determine the nature of the surface moieties, XPS was utilised. The resulting XPS data can be observed in Figure 3, where $\text{Mo}_2\text{TiC}_2\text{T}_x$ survey and core-level scans are seen in Figure 3A–D, ML- $\text{Ti}_3\text{C}_2\text{T}_x$ in Figure 3E–G, $\text{Ti}_3\text{C}_2\text{T}_x$ in Figure 3H–J and V_2CT_x in Figure 3K,L. From the survey scans, we can develop a general idea of the elemental (atomic) composition of the as-synthesised MXenes. When analysing this data, we will omit carbon contributions due to the high chance of adventitious carbon contamination. When normalised against Mo (3d), in $\text{Mo}_2\text{TiC}_2\text{T}_x$, we obtain an atomic percentage ratio of 1:0.3:0.64:0.05 for Mo:Ti:O:F.

The non-stoichiometric ratio between Mo and Ti deviates from observations in HAADF-STEM-EDS and is difficult to explain. A potential explanation is that the harsh etching process utilised could have resulted in the oxidation of carbon and titanium (forming TiO_2), forming internal point defects, resulting in titanium-deficient $\text{Mo}_2\text{TiC}_2\text{T}_x$. This reasoning could be supported by the fact that, in the core-level spectra of Ti 2p, we observe

the presence of $\text{TiO}_{2-x}\text{F}_{2x}/\text{TiO}_2$ states at 458.7 eV (464 eV, $2p_{1/2}$) contributing to 14.1% of the total Ti 2p bonding states. Additionally, Ti^{2+} (455.7 eV, 461.5 eV ($2p_{1/2}$)) has a contribution of 60.2% and Ti^{3+} (456.7 eV, 462.5 eV ($2p_{1/2}$)) has a contribution of 25.7% to the total bonding states of Ti.

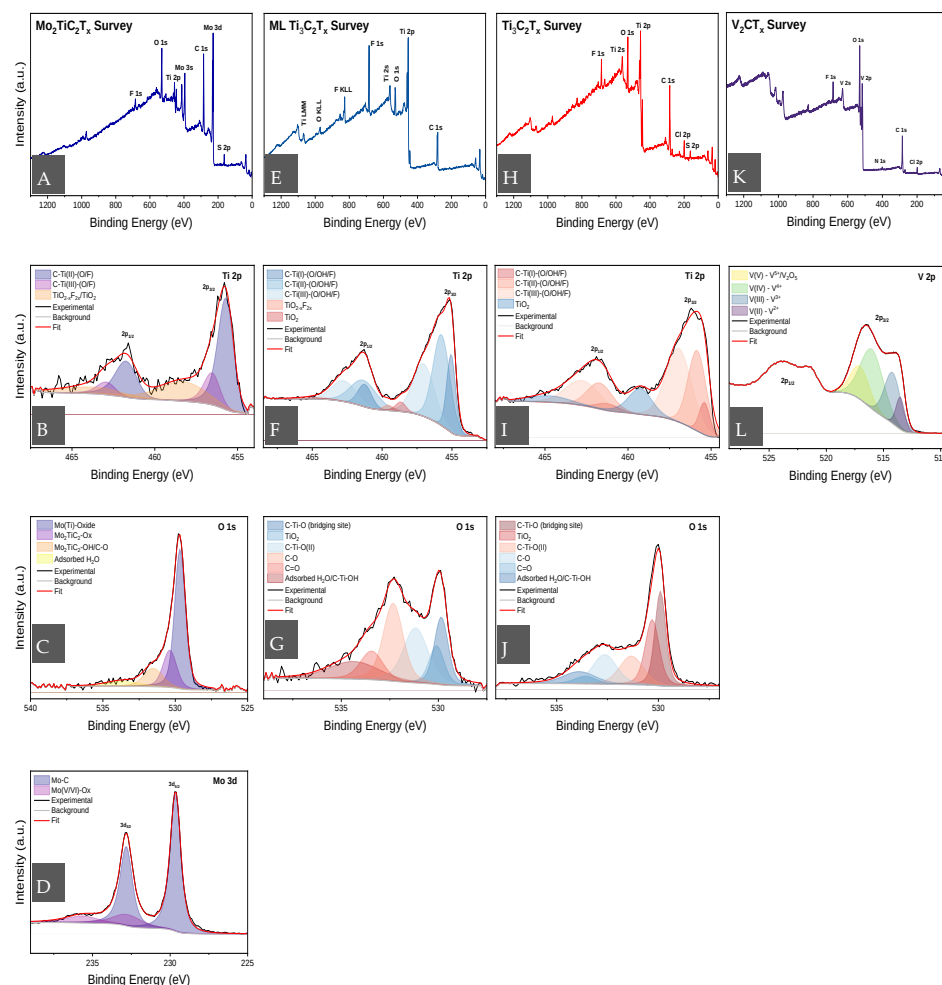


Figure 3. XPS of: (A) $\text{Mo}_2\text{TiC}_2\text{T}_x$ survey scans with core-level scans of (E) Ti 2p, (I) O 1s and (L) Mo 3d; (B) $\text{ML-Ti}_3\text{C}_2\text{T}_x$ survey scans with core-level scans of (F) Ti 2p and (J) O 1s; (C) delaminated $\text{Ti}_3\text{C}_2\text{T}_x$ survey scans with core-level scans of (G) Ti 2p and (K) O 1s; (D) V_2CT_x survey scans with core-level scan of (H) V 2p.

The core-level emission of Mo (3d) in $\text{Mo}_2\text{TiC}_2\text{T}_x$ exhibits a main peak at 229.6 eV (and 232.8 eV, $2p_{1/2}$) indicative of the Mo-C bond and is representative of 87% of the Mo bonding states. There is, however, a small presence of $\text{Mo}^{5+/6+}$ oxide, represented by the peaks at 232.6 eV and 235.5 eV ($2p_{1/2}$). The Mo-Ox bond represents only 13% of the total Mo bonding states. Thus, although the synthesis of $\text{Mo}_2\text{TiC}_2\text{T}_x$ was a success, a small amount of the MXene was also oxidised. With regard to oxygen-based functional groups, Mo(Ti)-oxide (530.1 eV), $\text{Mo}_2\text{TiC}_2\text{-O}_x$ (530.5 eV), adsorbed H_2O (533.5 eV) and $\text{Mo}_2\text{TiC}_2\text{-OH/C-O}$ (531.9 eV) were identified, representing 46.8%, 27.5%, 10% and 15.7%, respectively. The fluorine-based functional groups constitute a singular bonding state, C-(Mo,Ti)-F, at 685.4 eV. The F 1s component labelled as fluoride contamination corresponds to residual reaction by-products (e.g., LiF or other fluoride species) formed during the etching process, consistent with previous MXene reports. Although the C 1s peak is not typically used for quantification, it is interesting to note the presence of metal carbide peaks, Mo-C (282.2 eV) and Mo(Ti)-C (282.9 eV), as these peaks are typically used in the literature to determine the

successful synthesis of non-degraded MXenes [44]. We can also observe a strong Ti-C peak in ML-Ti₃C₂T_x (Figure S4D) and Ti₃C₂T_x (Figure S4F) at 282.2 eV. It is also interesting to observe that there is a stronger contribution of C-C and C-O in the MXenes synthesised via HF etching, as opposed to the MILD method. The total contributions of C-C and C-O in Mo₂TiC₂T_x and ML-Ti₃C₂T_x are 73.4% and 60.2%, respectively, whereas it is only 44.7% for Ti₃C₂T_x.

Comparing the elemental composition of ML-Ti₃C₂T_x and Ti₃C₂T_x, normalised with respect to titanium, we obtain the following atomic ratios: 1:0.45:0.43 (Ti:O:F) and 1:0.42:0.17:0.25 (Ti:O:F:Cl). With this, we observe a significantly higher fluoride content in ML-Ti₃C₂T_x but also a large amount of chloride being present in the Ti₃C₂T_x synthesised via the MILD method. Looking at the core-level spectra of Cl 2p, we determine that 77.4% of the bonding states are from Ti-Cl (199.4 eV, 201.1 eV (2p_{1/2})), with 22.6% attributed to potential chloride contamination (adsorbed chloride species and/or salts). In the F 1s core-level spectra, however, fluoride contamination (from reaction by-products or salts used) at 686.7 eV and 686.4 eV represents 38.3% of the fluoride bonding state in ML-Ti₃C₂T_x and only 24.3% in Ti₃C₂T_x, respectively. The other chemical state present is attributed to C-Ti-F₂O bonds, which are found at 685.4 eV.

From Figure 3G,J, we can observe that the distribution of oxygen bonding states differs between ML-Ti₃C₂T_x and Ti₃C₂T_x. A significant bond found for both MXenes is C-Ti-O, which is found at the bridging site of the MXene [44]. Found at 529.8 eV for ML-Ti₃C₂T_x and 529.9 eV for Ti₃C₂T_x, it represents 15.9% and 26.4% of the total oxygen bonding states, respectively (data summarised in Table S1). The rest of the bonding groups present TiO₂, adsorbed H₂O/C-Ti-OH, C-Ti²⁺-O, C-O and C=O constitutes 9.8% (530.1 eV), 14.8% (534.4 eV), 22.7% (531.2 eV), 26% (532.3 eV) and 10.8% (533.4 eV) and 23.7% (530.3 eV), 10.2% (533.9 eV), 17.4% (531.3 eV), 18.2% (532.6 eV) and 4.1% (533.6 eV) for ML-Ti₃C₂T_x and Ti₃C₂T_x, respectively. Looking at the Ti 2p core-level spectra, the presence and distribution of C-Ti¹⁺-(O/OH/F), C-Ti²⁺-(O/OH/F), C-Ti³⁺-(O/OH/F), TiO_{2-x}F_{2x} and TiO₂ are very similar. For ML-Ti₃C₂T_x these bonds are found at 455.1 (461.2(2p_{1/2})), 455.8 (461.3(2p_{1/2})), 457 (462.8(2p_{1/2})), 459.5 (464.6(2p_{1/2})) and 458.6 (464.6(2p_{1/2})) eV, respectively. They represent 19.7%, 43.7%, 32.1%, 1.5% and 3% of the total titanium bonding states present. For Ti₃C₂T_x, they can be found at 455.2 (461.2 (2p_{1/2})), 455.8 (461.5(2p_{1/2})), 457.1 (462.8(2p_{1/2})), 459.4 (464.6(2p_{1/2})) and 458.6 (464.6(2p_{1/2})) eV, respectively, representing 17.1%, 41%, 36.6%, 1.9% and 3.4% of the bonding states present. It should be noted that in both cases, the amounts of oxyfluoride and oxide species are very low and can be subjected to significant error in XPS interpretation. Thus, the takeaway should be qualitative, in that there is a very small amount of oxide present for both the ML-Ti₃C₂T_x and Ti₃C₂T_x, but it is insufficient to alter the overall chemical and physical properties of the MXene.

Finally, we can observe the XPS survey and core-level spectra of V₂CT_x in Figure 3L. Generally, the atomic ratio normalised to vanadium is determined to be 1:3.30:0.28:0.05:0.05 for V:O:F:Cl:N. The presence of nitrogen indicates a residual amount of amines present from the TMAOH utilised in the exfoliation stage of the synthesis. The significant ratio of oxygen to vanadium indicates a partial oxidation of the MXene. From the V 2p core-level spectra, we identify V⁵⁺ (517.5 eV, 2p_{3/2}), associated with V₂O₅, V⁴⁺ (516.5 eV, 2p_{3/2}), V³⁺ (514.3 eV, 2p_{3/2}) and V-C/V²⁺ (513.5 eV, 2p_{3/2}), representing 14.9%, 69.3%, 12.6% and 3.2%, respectively, of the total bonding states of vanadium. Low-valence vanadium, V²⁺ and V³⁺, are typically associated with V₂CT_x MXene, whilst higher-valence-state vanadium is typically indicative of oxides. Interestingly, previous work has found that as the outer surface of V₂CT_x is oxidised to a high-valence VO_x, the inner crystalline structure, i.e., V-C-V sheets, can be well preserved, leading to the formation of a V₂CT_x-VO_x heterostructure [45]. Based on the bonding state distribution observed in V 2p, this appears to be the dominant

chemical state of the MXene, i.e., a mixture of pristine V_2CT_x , $V_2CT_x-VO_x$ heterostructure and V_2O_5 . Overall, the XPS results obtained from the as-synthesised MXenes correspond with interpretations made in previous studies [17,44–52].

3.2. MXene Electrode Microstructure

Once the as-synthesised MXenes were characterised, they were cast onto copper foil current collectors for assembly in Li coin cells. The resulting electrode thicknesses were $33.1 \pm 1.2 \mu m$, $21.5 \pm 0.5 \mu m$, $11.3 \pm 0.7 \mu m$ and $51.5 \pm 0.9 \mu m$ for V_2CT_x , $Mo_2TiC_2T_x$, $Ti_3C_2T_x$ and $ML-Ti_3C_2T_x$ electrodes, respectively. The significantly thinner $Ti_3C_2T_x$ electrode suggests significant re-stacking of the MXene, resulting in a dense film-like electrode. The differing morphologies of the respective MXene electrodes can be observed in Figure 4. In Figure 4A–C, we can observe the V_2CT_x electrodes. The surface of the electrode is rough and appears to have a high degree of porosity. Upon closer inspection, in Figure 4B, we can observe sub-micron particulates that are homogeneously dispersed on a matrix. This appears to be the potential $V_2CT_x-VO_x$ heterostructure identified from XPS. It is challenging to resolve, at any degree of magnification, existing V_2CT_x scrolls within the electrode. Therefore, a conclusion is that, due to the poor stability of pristine V_2CT_x , the majority of the MXene has converted into a combination of $V_2CT_x-VO_x$ heterostructures and VO_x . SEM-EDS in Figure S5D illustrates the homogeneous dispersion of vanadium in the electrode, as well as oxygen, carbon, chlorine and fluorine. In Figure 4E, we observe the morphology of the $Mo_2TiC_2T_x$ electrode, which appears to resemble dense clusters of re-stacked sheets. Comparatively, the $Ti_3C_2T_x$ electrode in Figure 4G appears to have formed a dense film with no observable pores, confirming the high degree of re-stacking of the $Ti_3C_2T_x$ sheets.

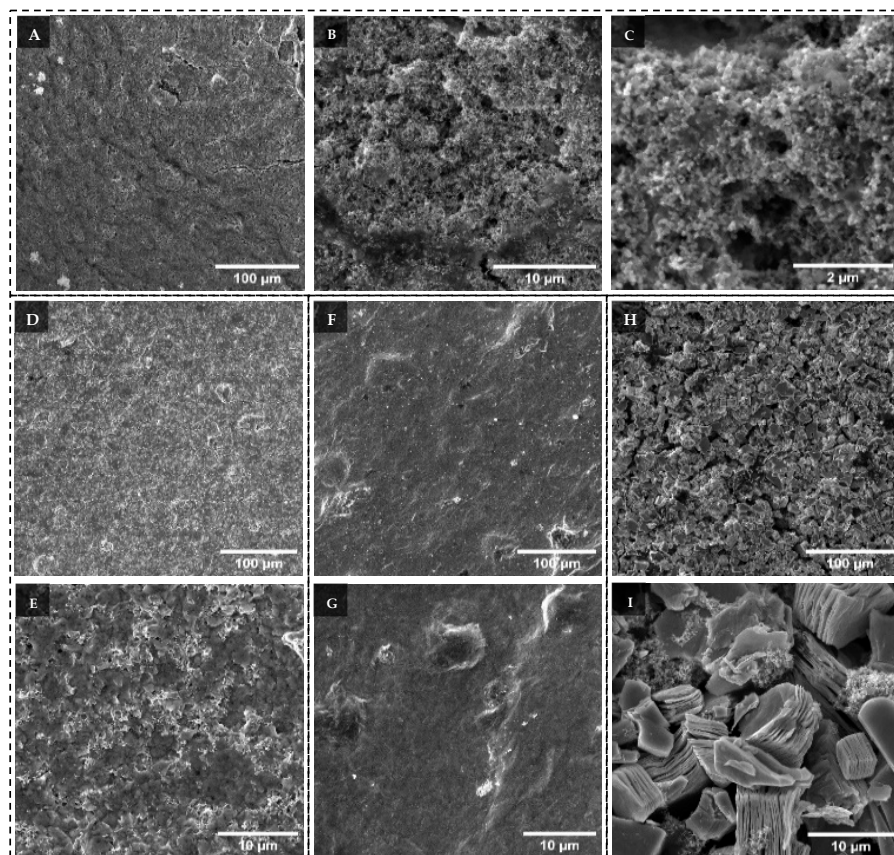


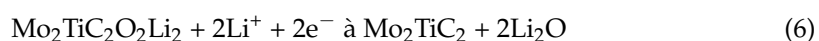
Figure 4. SEM micrographs of (A) V_2CT_x electrodes at low, (B) intermediate and (C) high magnifications; (D) $Mo_2TiC_2T_x$ electrodes at low and (E) intermediate magnifications; (F) $Ti_3C_2T_x$ electrodes at low and (G) intermediate magnifications; (H) $ML-Ti_3C_2T_x$ at low and (I) intermediate magnifications.

An explanation for the different electrode morphologies observed between $\text{Mo}_2\text{TiC}_2\text{T}_x$ and $\text{Ti}_3\text{C}_2\text{T}_x$, despite them being isostructural MXenes, could be attributed to their lateral dimensions, which differ by an order of magnitude (or more). The significantly smaller $\text{Mo}_2\text{TiC}_2\text{T}_x$ sheets (broken sheets due to the rigorous exfoliation steps used in the synthesis), when formed into the electrode, are unable to overlap and stack in a continuous manner, resulting in voids and porosity developing throughout the microstructure of the electrode. On the other hand, the larger, more pristine sheets of $\text{Ti}_3\text{C}_2\text{T}_x$ form a continuous lay-up of sheets, with their lateral size being sufficient to occlude the space between neighbouring $\text{Ti}_3\text{C}_2\text{T}_x$ sheets. This results in a densely stacked $\text{Ti}_3\text{C}_2\text{T}_x$ electrode, with no voids or porosity present. Despite the difference in morphology, we can observe in Figure S4A–D that the dispersion of MXene and binders is homogeneous throughout the electrode, although there appears to be a cluster of $\text{Mo}_2\text{TiC}_2\text{T}_x$ still present in the $\text{Mo}_2\text{TiC}_2\text{T}_x$ electrode. Finally, in Figure 4I, we can observe the ML- $\text{Ti}_3\text{C}_2\text{T}_x$ electrode morphology in which the ML- $\text{Ti}_3\text{C}_2\text{T}_x$ particles are interspersed with Super P conductive additive and binders. The electrode appears to have a significant number of voids and porosity formed between the MXene particles. This electrode microstructure morphology is more commonly observed in commercial electrodes, as opposed to the previously discussed MXene electrodes.

3.3. Electrochemical Performance of MXene Electrodes

Cyclic Voltammetry (CV): With the as-prepared MXenes and electrodes characterised, we can now evaluate the electrochemical performance in lithium half-cells. Figure 5 illustrates the cyclic voltammetry of the respective MXene electrodes at various scan rates between 0.1 mV s^{-1} and 2.0 mV s^{-1} (Figure 5A–D) to evaluate diffusion-dominated charge storage mechanisms and between 5 mV s^{-1} and 100 mV s^{-1} (Figure 5E–H) to look further into capacitance-dominated charge storage mechanisms.

Firstly, it should be noted that as it is a half-cell, the lithiation process occurs as the potential is swept from 3 V to 0.01 V, whilst the de-lithiation process occurs when the potential is swept from 0.01 V to 3 V. In the lithiation sweep of the $\text{Mo}_2\text{TiC}_2\text{T}_x$, ML- $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Ti}_3\text{C}_2\text{T}_x$ electrodes, we see a broad and shallow peak roughly between 0.5 V and 1.25 V. This is seen prominently in the CV curve of ML- $\text{Ti}_3\text{C}_2\text{T}_x$ in Figure 5B, together with a shallower and broader peak at roughly 1.5 V. This peak can also still be observed for $\text{Mo}_2\text{TiC}_2\text{T}_x$, as seen in Figure 5A, and for the lower scan rates of $\text{Ti}_3\text{C}_2\text{T}_x$, but it virtually disappears at higher scan rates. This peak, together with the pronounced peak observed in the de-lithiation sweep between 1.25 V and 2.5 V, can be associated with intercalation of Li^+ and partial surface-mediated redox reactions [53]. These peaks are most pronounced on the ML- $\text{Ti}_3\text{C}_2\text{T}_x$ and $\text{Ti}_3\text{C}_2\text{T}_x$, suggesting that this is the dominant charge storage mechanism. However, the lack of a strong current response as compared to ML- $\text{Ti}_3\text{C}_2\text{T}_x$ during lithiation, suggest the difficulty of lithium diffusion into the $\text{Ti}_3\text{C}_2\text{T}_x$ electrode potentially attributed to the dense re-stacking. This is also potentially why we observe a broader and shallower peak for $\text{Ti}_3\text{C}_2\text{T}_x$ in the de-lithiation sweep due to the difficulty in extraction of intercalated Li^+ ions. This does not appear to be an issue the ML- $\text{Ti}_3\text{C}_2\text{T}_x$ faces, as the voids and porosity present between the ML- $\text{Ti}_3\text{C}_2\text{T}_x$ particles allow for the rapid diffusion of Li^+ through the electrode and into/out of the MXene particles. On the other hand, the peaks associated with (de)intercalation are not as prominent for the $\text{Mo}_2\text{TiC}_2\text{T}_x$ MXene, suggesting that it is not the main charge storage mechanism. Previous studies [16,17] have demonstrated that the primary charge storage mechanism for $\text{Mo}_2\text{TiC}_2\text{T}_x$ is a conversion reaction(s) outlined in the equation below:



In effect, the Mo-O groups present on the surface of the MXene, which XPS has confirmed is a dominant moiety, undergo a lithiation reaction, as seen in Equation (5). This lithiated MXene is then able to undergo an additional conversion reaction with a further two moles of lithium, as seen in Equation (6). These might be the reactions associated with the peaks observed between 0.5 V and 1.25 V during lithiation and de-lithiation.

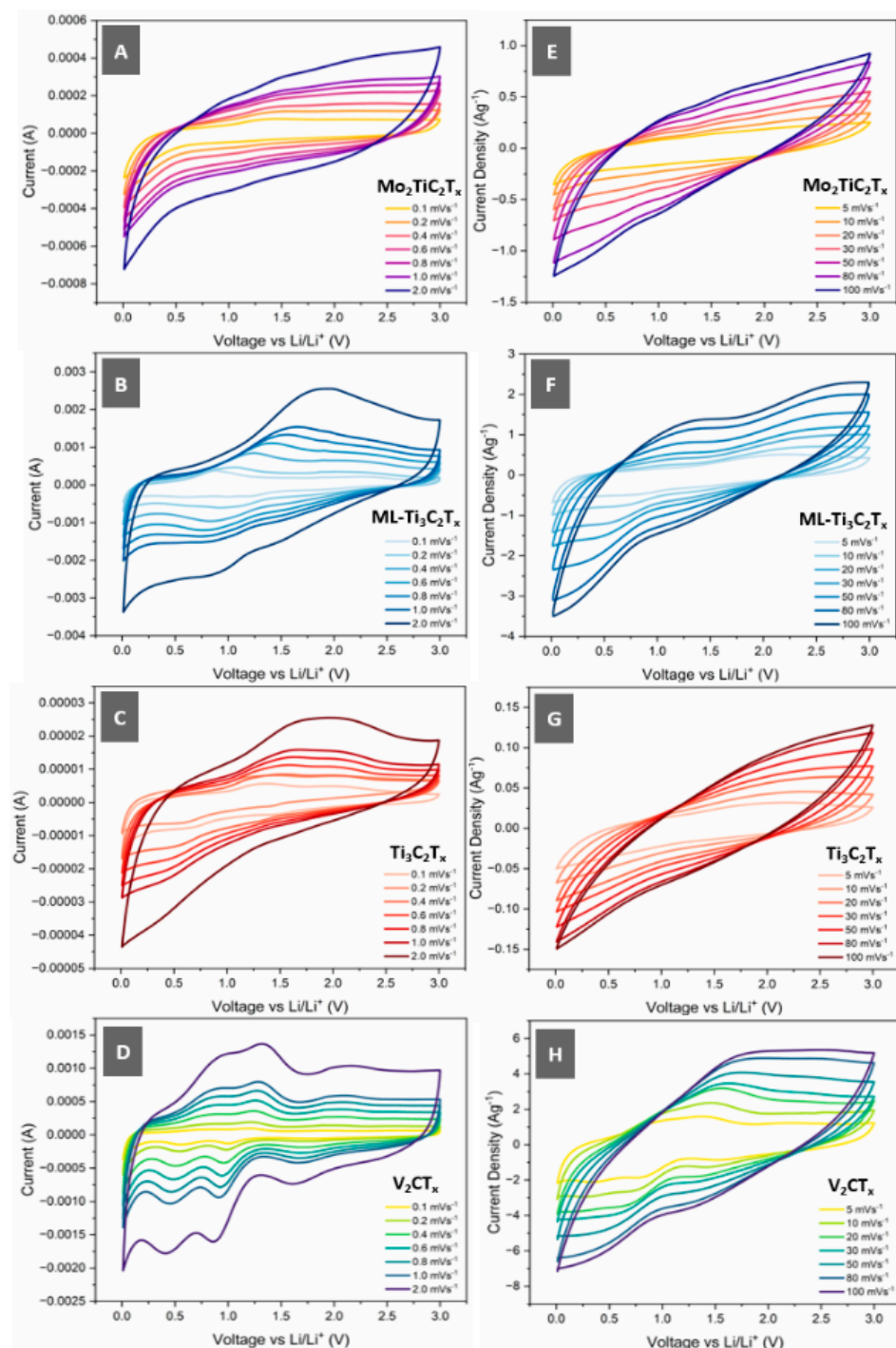
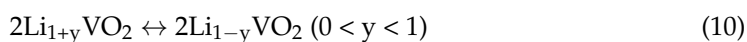
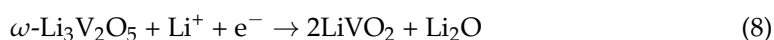
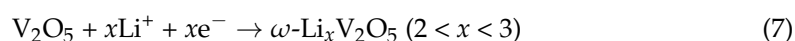


Figure 5. Cyclic voltammetry (CV) of $\text{Mo}_2\text{TiC}_2\text{T}_x$ (A), $\text{ML-Ti}_3\text{C}_2\text{T}_x$ (B), $\text{Ti}_3\text{C}_2\text{T}_x$ (C) and V_2CT_x (D) MXene electrodes between the scan ranges of 0.1–2.0 mVs^{-1} and (E–H) 5–100 mVs^{-1} between the voltage range of 0.01 V to 3.0 V in lithium half-cells (coin).

The enthalpy changes occurring in Equation (6) make it energetically favourable for the $\text{Mo}_2\text{TiC}_2\text{O}_2$ MXene to undergo the reaction, whereas it is not so for $\text{Ti}_3\text{C}_2\text{O}_2$ MXenes,

which is why we do not observe this as being the dominant charge mechanism for the ML-Ti₃C₂T_x and Ti₃C₂T_x electrodes [16].

In Figure 5D, we can observe that the CV profile of V₂CT_x-VO_x electrodes differs substantially from those of the other MXenes. We still observe broad shallow peaks at roughly 1.6 V in the lithiation sweep and 2 V in the de-lithiation sweep, which could be attributed to intercalation/diffusion of Li⁺ into existing V₂CT_x scroll structures and potentially surface-mediated redox reactions [53]. However, in addition to these peaks, we observe lithiation peaks at roughly 0.5 V and 1 V, as well as de-lithiation peaks at 0.8 V and 1.25 V. These correspond well to a VO₂ lithiation/de-lithiation process discovered in previous work [54,55]. In previous work, Bo Yan et al. [54] experimentally validated the following (de)lithiation process:



Equations (7)–(9) represent the lithiation of a V₂O₅ species into a lithiated Li_{1+y}VO₂ compound within the first lithiation/de-lithiation cycle. Subsequently, the predominant conversion reaction occurring is represented in Equation (10). Although this reaction mechanism elucidates the redox events observed in the CV of the V₂CT_x-VO_x electrode and is further supported by the attainable specific capacity, further post-mortem and “in-situ” work should be conducted to empirically verify this charge storage mechanism.

Figure 5E–H demonstrate CV profiles of the MXene electrodes at high scan rates to evaluate their respective capacitive characteristics. Although capacitive charge storage via electrochemical double-layer capacitance (EDLC) is present at the lower scan rates, by increasing the scan rate, we reduce the diffusive charge storage contributions, and this will enable us to determine the capability of the MXene electrodes to function as pseudo-capacitor and/or supercapacitor electrodes. From the CV plots, we can calculate the attainable specific gravimetric capacitance, which is plotted in Figure S6.

Between the MXene electrodes, we observe similar decay in specific capacitance with scan rate. V₂CT_x-VO_x obtained the highest specific capacitance of 532.4 F g^{−1} at 2 mV s^{−1}, reducing to 381 F g^{−1} at 5 mV s^{−1} and 51.1 F g^{−1} at 100 mV s^{−1}. The ML-Ti₃C₂T_x electrode exhibited a maximum specific capacitance of 151.9 F g^{−1} at 2 mV s^{−1} that diminished to 18.8 F g^{−1} at 100 mV s^{−1}. Surprisingly, the worst performer was the Ti₃C₂T_x electrode, which managed 9.7 F g^{−1} at 2 mV s^{−1} and a negligible capacity of 0.73 F g^{−1} at 100 mV s^{−1}.

The observed performance of the electrodes can be attributed to the chemistry and structure of the respective MXenes. In Figure 5H, we observe that despite the high scan rate, there are still some pseudocapacitive reactions occurring which might be associated with surface redox reactions and intercalation events. This phenomenon holds true for the Mo₂TiC₂T_x electrode, although the poorer observed capacitance might be attributed to slower reaction kinetics in the formation of Li₂O, as seen in Equation (6). Surprisingly, the ML-Ti₃C₂T_x managed a greater capacitive performance compared to the Mo₂TiC₂T_x, which could be attributed to the low tortuosity and open morphology of the electrode, allowing for rapid diffusion and intercalation of Li⁺. The poor capacitive performance of Ti₃C₂T_x in this context can be associated with its highly dense re-stacked morphology. This reduces the effective electrochemically active surface area (to the top surface of the electrode) as the rest of the electrode bulk is only accessible via highly tortuous and narrow ion diffusion pathways. As a result, when the cell was subject to galvanostatic cycling, it

regularly exceeded voltage thresholds and thus was not able to be characterised further. It is important to note that this is not representative of the electrochemical performance of $\text{Ti}_3\text{C}_2\text{T}_x$, as previous work [47,48,56] has demonstrated state-of-the-art capacitive performance. However, it does highlight the importance of selecting a suitable manufacturing process to leverage the performance benefits that a 2D material might offer.

Galvanostatic Charging and Discharging (GCD): Following cyclic voltammetry measurements, the cells were galvanostatically cycled. As it is difficult to determine the exact nominal capacity of the MXene materials, the electrodes were subjected to fixed current densities between 50 mA g^{-1} to 2 A g^{-1} . Figure 6 demonstrates the results from galvanostatic cycling of the MXene electrodes, including the voltage profiles, rate capability and cycling stability. In Figure 6A, we can observe the voltage profile of $\text{Mo}_2\text{TiC}_2\text{T}_x$. Unlike $\text{ML-Ti}_3\text{C}_2\text{T}_x$ and $\text{V}_2\text{CT}_x\text{-VO}_x$, it appears that a significant proportion of the electrode capacity comes from below 0.6 V. This is consistent with previous work [16] in which the charge storage mechanism is a conversion reaction represented by Equations (5) and (6). The voltage profile of $\text{ML-Ti}_3\text{C}_2\text{T}_x$ in Figure 6B is characteristic of an intercalation mechanism, whilst in Figure 6C, the voltage profile of $\text{V}_2\text{CT}_x\text{-VO}_x$ has several short and shallow plateaus, which is evidence of the lithiation/de-lithiation reaction demonstrated in Equation (10). $\text{Mo}_2\text{TiC}_2\text{T}_x$ has the worst rate capability (capacity retention) amongst the three electrodes. It achieved $391.7 \text{ mA h g}^{-1}$ at 50 mA g^{-1} , $297.2 \text{ mA h g}^{-1}$ at 100 mA g^{-1} , 96.1 mA h g^{-1} at 300 mA g^{-1} , 50.6 mA h g^{-1} at 500 mA g^{-1} , 24.4 mA h g^{-1} at 1 A g^{-1} and 15.6 mA h g^{-1} at 2 A g^{-1} . This indicates a 96% drop in specific capacity as the current density is increased. The $\text{ML-Ti}_3\text{C}_2\text{T}_x$ electrode achieved 92.8 mA h g^{-1} at 50 mA g^{-1} , 73.8 mA h g^{-1} at 100 mA g^{-1} , 36.4 mA h g^{-1} at 300 mA g^{-1} , 22.3 mA h g^{-1} at 500 mA g^{-1} , 14.9 mA h g^{-1} at 1 A g^{-1} and 10.4 mA h g^{-1} at 2 A g^{-1} , which represents an 89% drop in specific capacity. This is still a significant decay, but slightly less so than $\text{Mo}_2\text{TiC}_2\text{T}_x$. The $\text{V}_2\text{CT}_x\text{-VO}_x$ electrode managed the highest capacity of $493.3 \text{ mA h g}^{-1}$ at 50 mA g^{-1} , $430.7 \text{ mA h g}^{-1}$ at 100 mA g^{-1} , 336 mA h g^{-1} at 300 mA g^{-1} , $267.3 \text{ mA h g}^{-1}$ at 500 mA g^{-1} , 164 mA h g^{-1} at 1 A g^{-1} and 65.3 mA h g^{-1} at 2 A g^{-1} . The electrode demonstrated an improved rate capability at intermediate current densities but still suffered from an 87% decay in capacity as current density was increased. The large decay in the specific capacity of the respective electrodes could be attributed to the low density and poor inter-particle contact in the electrode, resulting in lower electronic conductivity. It can be improved with electrode engineering approaches such as the addition of more conductive binder, reducing particle size (in the context of $\text{ML-Ti}_3\text{C}_2\text{T}_x$) or calendaring the electrode post-drying. The poor rate capability of $\text{Mo}_2\text{TiC}_2\text{T}_x$ especially could also be attributed to poor reaction (Equations (5) and (6)) kinetics leading to a lower attainable specific charge capacity.

All three electrodes demonstrated respectable cycling stability across 200 cycles. The $\text{V}_2\text{CT}_x\text{-VO}_x$ demonstrated the best cycling stability when cycled at 150 mA g^{-1} , starting at $339.2 \text{ mA h g}^{-1}$ and decaying by 14.2% (0.071% per cycle) after 200 cycles. The $\text{ML-Ti}_3\text{C}_2\text{T}_x$ demonstrated the worst cycling stability, decaying by 25.8% (0.129% per cycle) across 200 cycles when cycled at 50 mA g^{-1} . The $\text{Mo}_2\text{TiC}_2\text{T}_x$ fared slightly better when cycled at 50 mA g^{-1} , starting at $430.5 \text{ mA h g}^{-1}$ and decaying by 21.8% (0.109% per cycle) across the 200 cycles.

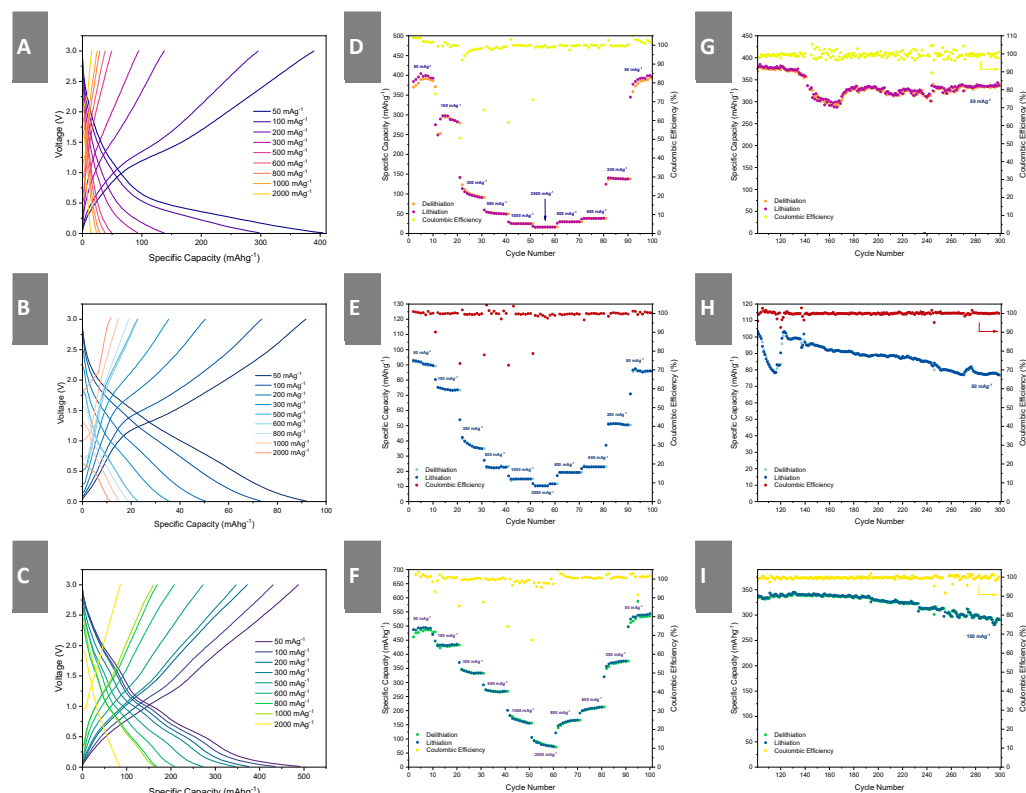


Figure 6. Galvanostatic plots demonstrating the voltage profiles (A–C), rate performance (D–F) and cycling stability (G–I) of Mo₂TiC₂T_x, ML-Ti₃C₂T_x and V₂CT_x, respectively, under galvanostatic charge and discharge cycles.

4. Conclusions

This work has demonstrated the successful synthesis of Mo₂TiC₂T_x and multi-layer Ti₃C₂T_x via the commonly used HF etching method. Delaminated Ti₃C₂T_x and V₂CT_x were also successfully synthesised using a modified minimally invasive layer delamination (MILD) method. An unprecedented discovery was the formation of pristine mono-layer scrolls of V₂CT_x, which is a novel morphology for as-synthesised MXenes. The as-synthesised MXenes were prepared into electrodes and evaluated in lithium half-cells as anodic and pseudo-capacitor electrodes. It was discovered that, in the preparation of these electrodes, the V₂CT_x naturally oxidised due to poor stability under ambient conditions, resulting in the formation of V₂C-VO_x heterostructures, as validated by SEM, XPS and lithiation behaviour. From electrochemical characterisation, we have evaluated the varying lithiation mechanisms of the various MXenes, concurring that both MXene transition metal chemistry and nanomaterial morphology significantly impact the resultant electrochemical performance. The Mo₂TiC₂T_x MXene lithiation mechanism involves the conversion reaction of Li⁺ with surface Mo-O groups, leading to the formation of Li₂O. On the other hand, the redox behaviour of isostructural Ti₃C₂T_x (and ML-Ti₃C₂T_x) indicates lithiation occurs more often through an intercalation process with some surface-mediated redox reactions. The V₂CT_x-VO_x heterostructure appears to undergo a mixture of conversion reactions via formation of Li_{1-y}VO₂ as well as intercalation into the remaining scroll-like V₂CT_x structures. It has also been discovered that the morphology of the respective MXenes led to the formation of electrodes with significantly varying morphology. The smaller lateral size of Mo₂TiC₂T_x mitigated extensive re-stacking, forming porosity that can act as accessible ion channels, whereas the large lateral size of Ti₃C₂T_x created a dense film of re-stacked MXene, reducing the accessible electrochemically active surface area. The particulate nature of ML-Ti₃C₂T_x with void space interspersed also allowed for ion diffusion and rapid Li⁺

intercalation. The hope is that this work will serve as an informative guide toward the future development of MXene composite materials for battery and supercapacitor materials via the development of a more comprehensive understanding of how the intrinsic chemistry and structure of the as-synthesised MXene, without further processing, can directly impact electrochemical energy storage device performance.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/esa2040016/s1>.

Author Contributions: F.P.M. designed the project and conducted the majority of the experimentation and analysis involved, namely material synthesis; electrode fabrication; cell preparation; cell electrochemical testing and analysis; SEM, XRD, TEM, HRTEM, STEM-EDS, SAED, XPS sample preparation, testing and analysis. Y.G. synthesised the V2CTx MXenes utilised, providing the SEM micrographs, XPS and XRD data associated with the batch. Y.S. experimentally conducting the TEM, HRTEM, STEM and HAADF-STEM-EDS on the as-prepared samples and providing guidance on the respective analysis. M.A.B. contributed to review and editing, validation, supervision and resources. This work is part of F.P.M. and Y.G.'s Doctoral thesis [57,58]. All authors have read and agreed to the published version of the manuscript.

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