Mixed MXenes: Mo$_{1.33}$CT$_2$ and Ti$_3$C$_2$T$_2$ freestanding composite films for energy storage

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**ABSTRACT**

MXenes are a class of 2D materials with outstanding properties, including high electronic conductivity, hydrophilicity, and high specific capacitance. In particular, Mo$_{1.33}$CT$_2$ MXene has a high specific capacitance, whereas films of Ti$_3$C$_2$T$_2$ MXene possess high flexibility and high electronic conductivity. The fabrication of composite materials based on these two MXenes is therefore motivated, taking advantage of combining their good properties. In this article, we introduce a one-step approach to prepare composite MXene films using pristine Mo$_{1.33}$CT$_2$ and Ti$_3$C$_2$T$_2$ MXenes. The composite films display superior flexibility and electronic conductivity, as well as high capacitance, up to 1380 F cm$^{-2}$ (460 F g$^{-1}$), in 1 M H$_2$SO$_4$. A capacitance retention of 96% is obtained after 17,000 cycles. In addition, the capacitance retentions are about 56% and 25% at scan rates of 200 mV s$^{-1}$ and 1000 mV s$^{-1}$, respectively. A significant rise in the capacitance at high rates, 875 F cm$^{-2}$ (282 F g$^{-1}$) at a current density of 20 A g$^{-1}$, is achieved by using a 3 M H$_2$SO$_4$ solution. The use of composite MXene as negative electrodes for asymmetric supercapacitor devices, as well as lithium-ion batteries, is also discussed. This work suggests new pathways for the use of MXene composites with double transition metals (Mo and Ti) in energy storage devices.

1. Introduction

Nowadays, rechargeable energy storage devices, such as batteries and supercapacitors, are of great importance in our daily life due to their use in portable devices, electric vehicles, and wearable electronics. Therefore, ongoing exploration targets either improvement in the performance of currently available materials, or the discovery of novel materials. MXenes, discovered 10 years ago, are considered one of the most promising materials for energy storage. They have a general formula of M$_n$+1X$_n$T$_z$, where M = transition metal (e.g. Ti, Mo, V, Nb, Ta, etc.), X= C and/or N, and T = surface termination groups (e.g. OH, F, Cl, or O) [1,2] which can significantly influence the electronic, structural, and electrochemical properties of the MXene films [3-5]. MXenes are typically prepared from their parent 3D MAX phase with the general formula M$_n$+1AX$_n$, where A is typically Al [6]. Chemical etching using acid [1], molten salt [7], or ionic liquids [8] are approaches used for the selective removal of A elements from MAX phases. MXenes have various application-inspiring properties, including high electronic conductivity, tunable mechanical and tribological properties [9], and high gravimetric and volumetric capacitances [10-13]. Therefore MXenes have been explored for various applications, such as sensors [14,15], metal-ion capacitors [16,17], plasmonic devices [18,19], hydrogen evolution catalysts [20,21], water purification [22], sorbents for urea removal [23], electromagnetic interference shielding [24], metal-ion batteries [25,26], and supercapacitors [27-29].

MXenes have previously shown outstanding potential for energy storage applications [30], and various approaches have been developed to improve and tune the electrochemical performance of MXenes, including the formation of composite materials with carbon-based materials (e.g. graphene, graphene oxide, carbon nanotubes) [31-33], transition metal oxides [34], or transition metal chalcogenides [35]. Alternatively, other modifications can be employed to increase the MXene film porosity [36,37] and reduce the restacking of MXene flakes during vacuum filtration, such as freeze drying, [12,27] natural sedimentation [38], blade coating [39], template digestion [29], fast gelation [40], and laser writing [41]. Recently, composite materials constructed from Ti$_3$C$_2$T$_2$ MXene and nanostructured Nb-based carbides (e.g. Nb$_2$CT$_2$ MXene) [42] or nitrides (e.g. NbN nanoparticles) [43] have been reported, which show enhanced performance in supercapacitor applications (low rate capacitance of about 370 F g$^{-1}$ for...
The as prepared Mo$_{1.33}$CT$_2$ MXene films were brittle (Fig. 2a) and showed a relatively low electronic conductivity (about $1 \text{ S cm}^{-1}$, Fig. S2a) [52]. In contrast, the Ti$_3$C$_2$T$_x$ films featured high flexibility (see Fig. 2e and its inset), as well as a high electronic conductivity ($3400 \text{ S cm}^{-1}$, not shown). The detailed morphology and structure of the pristine MXenes, Mo$_{1.33}$CT$_2$ and Ti$_3$C$_2$T$_x$, have been described elsewhere [10,45,46], although the single-sheet materials have average lateral dimensions of approximately a few hundred nanometers for both Mo$_{1.33}$CT$_2$ and Ti$_3$C$_2$T$_x$. Upon adding 75% (weight%) of Mo$_{1.33}$CT$_2$ to 25% of Ti$_3$C$_2$T$_x$, the composite film that was formed, hereafter referred to as 3Mo:1Ti, showed an enhanced electronic conductivity of about 2.5 $\text{ S cm}^{-1}$, as determined by 4-point probe measurements (see Fig. S2a). Furthermore, the 3Mo:1Ti film displayed higher flexibility and better handling than the as-prepared Mo$_{1.33}$CT$_2$ MXene film (Fig. 2b and its inset). Likewise, the mixing of 50% (weight%) Mo$_{1.33}$CT$_2$ and 50% Ti$_3$C$_2$T$_x$ resulted in the formation of a flexible MXene film (see Fig. 2c and its inset), referred to as the 1Mo:1Ti film; with even higher electronic conductivity (about 140 $\text{ S cm}^{-1}$, Fig. S2a). These electronic conductivity values for the composite MXene films exceed the previously reported conductivity values for a Mo$_{1.33}$CT$_2$ MXene composite with PEDOT:PSS conducting polymer (18 $\text{ S cm}^{-1}$, Fig. S2a) [49]. It is clear that, as the percentage of the highly conducting Ti$_3$C$_2$T$_x$ MXene increases, the lower the electronic conductivity increases. However, when 25% (weight%) of Mo$_{1.33}$CT$_2$ was added to 75% of Ti$_3$C$_2$T$_x$, agglomeration of the laminated flakes was observed (see Fig. 2i) and a corrupted film was formed, limiting its practical application (see Fig. 2d). Fig. S2g shows a schematic illustration of the composition ratios of the prepared composite MXene films and the trend in agglomeration.

The Ti$_3$C$_2$T$_x$ and Mo$_{1.33}$CT$_2$ MXenes were produced using different etching approaches and different delaminating agents: LiCl and TBAOH, respectively (see experimental section). In order to understand the reason behind the agglomeration, we therefore investigated the effect of presence of such agents on the MXenes, by adding excess amount of TBAOH and LiCl to the Ti$_3$C$_2$T$_x$ and Mo$_{1.33}$CT$_2$ MXenes, respectively. Interestingly, the agglomeration was only observed upon adding excess LiCl to Mo$_{1.33}$CT$_2$ MXene, whereas the addition of excess TBAOH to Ti$_3$C$_2$T$_x$ MXene did not cause agglomeration (see Figs. S2k and l). Accordingly, the agglomeration observed in the 1Mo:3Ti sample can be attributed to the excess amount of LiCl originating from the etching procedure of the Ti$_3$C$_2$T$_x$ MXene, causing agglomeration to the Mo$_{1.33}$CT$_2$ MXene [55]. In other words, Ti$_3$C$_2$T$_x$ MXene can possibly act as a binder to the Mo$_{1.33}$CT$_2$ MXene in the 3Mo:1 T film [56], resulting in the formation of a flexible, freestanding, mixed MXene electrode. However, when the concentration of Ti$_3$C$_2$T$_x$ increases, the possibility of Mo$_{1.33}$CT$_2$ agglomeration increases due to the presence of a greater amount of residual LiCl in the mixture, and thus agglomeration occurs for the film with the 1Mo:3Ti ratio. Care should therefore be taken when preparing mixed MXene films owing to the complicated aqueous chemistry of MXenes [57-59]. Future studies are motivated to address the agglomeration by using a similar delaminating agents for the two MXenes. To further investigate the origin of the agglomeration, XPS analysis was applied to the different composite MXene films. The XPS analysis was applied to the different composite MXene films. The XPS analysis was applied to the different composite MXene films. The XPS analysis was applied to the different composite MXene films. The XPS analysis was applied to the different composite MXene films.

The aqueous suspensions of Mo$_{1.33}$CT$_2$ and Ti$_3$C$_2$T$_x$ MXenes were mixed by hand shaking in given weight ratios, which after vacuum filtration produced a series of Mo$_{1.33}$CT$_2$-Ti$_3$C$_2$T$_x$ composite films (see Table 1). The overall film loadings were about 2.1 mg cm$^{-2}$, which can be considered relatively high. It should be noted that hand shaking has the advantage over other approaches such as magnetic stirring or sonication, because it is simple, fast, straightforward, and decrease the chance of oxidation of MXenes or formation of MXene flakes with small flake size.[54].
**Table 1** Summary of the composite $\text{Mo}_{1.33}\text{CT}_2$-Ti$_2$C$_2$T$_6$ electrodes prepared in this study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{Mo}_{1.33}\text{CT}_2$</th>
<th>$\text{Ti}_2\text{C}_2\text{T}_6$</th>
<th>Loading (mg cm$^{-2}$)</th>
<th>Film Thickness ($\mu$m)</th>
<th>Overall electrode mass (4 mm diameter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mo}_{1.33}\text{CT}_2$</td>
<td>20 ml (1.0 mg ml$^{-1}$)</td>
<td>–</td>
<td>–</td>
<td>2.1 ($\pm$ 0.1)</td>
<td>6.0 ($\pm$ 0.5)</td>
</tr>
<tr>
<td>3Mo:1Ti</td>
<td>15 ml (1.0 mg ml$^{-1}$)</td>
<td>75</td>
<td>5 ml (1 mg ml$^{-1}$)</td>
<td>25</td>
<td>2.1 ($\pm$ 0.1)</td>
</tr>
<tr>
<td>3Mo[$\text{Y}:1\text{Ti}$*]</td>
<td>15 ml (1.0 mg ml$^{-1}$)</td>
<td>75</td>
<td>5 ml (1.0 mg ml$^{-1}$)</td>
<td>25</td>
<td>2.1 ($\pm$ 0.1)</td>
</tr>
<tr>
<td>1Mo:1Ti</td>
<td>10 ml (1.0 mg ml$^{-1}$)</td>
<td>50</td>
<td>10 ml (1 mg ml$^{-1}$)</td>
<td>50</td>
<td>2.1 ($\pm$ 0.1)</td>
</tr>
<tr>
<td>1Mo:3Ti</td>
<td>5 ml (1.0 mg ml$^{-1}$)</td>
<td>25</td>
<td>15 ml (1.0 mg ml$^{-1}$)</td>
<td>75</td>
<td>2.1 ($\pm$ 0.1)</td>
</tr>
<tr>
<td>Ti$_2$C$_2$T$_6$</td>
<td>–</td>
<td>–</td>
<td>20 ml (1.0 mg ml$^{-1}$)</td>
<td>100</td>
<td>2.1 ($\pm$ 0.1)</td>
</tr>
</tbody>
</table>

*aPrepared from $[\text{Mo}_{2.3}\text{Y}_{1.0}]/\text{AlC-f-MAX}$ phase.

**Fig. 2.** Morphology of $\text{Mo}_{1.33}\text{CT}_2$-Ti$_2$C$_2$T$_6$ composite MXene films: (a–e) photos of the $\text{Mo}_{1.33}\text{CT}_2$, 3Mo:1Ti, 1Mo:1Ti, 1Mo:3Ti, and Ti$_2$C$_2$T$_6$ films, respectively. The inset images in (b), (c), and (e) show the bent state of the 3Mo:1Ti, 1Mo:1Ti, and Ti$_2$C$_2$T$_6$ films, illustrating their flexibility. (f–h) and (j) show SEM cross-section images of the $\text{Mo}_{1.33}\text{CT}_2$, 3Mo:1Ti, 1Mo:1Ti, and Ti$_2$C$_2$T$_6$ films, respectively. (i) Photo of the 1Mo:3Ti suspension showing the agglomeration of MXene flakes after direct mixing.

survey spectra and the C 1s XPS spectra of the pristine and composite MXene samples are shown in Note S1. Fig. 3a and b show the XPS spectra of Ti 2p regions and Mo 3d regions for the composite films. Notably, the Ti 1Mo:1Ti and 3Mo:1Ti films displayed similar oxide levels for both Ti$_2$C$_2$T$_6$ and $\text{Mo}_{1.33}\text{CT}_2$ (see Table S4). However, the 1Mo:3Ti film showed the same oxide percentage for Ti$_2$C$_2$T$_6$, but a higher oxide content for the $\text{Mo}_{1.33}\text{CT}_2$ (the value increased from ≈10–47%). The latter observation suggests that the agglomeration observed in the 1Mo:3Ti sample can, also be attributed to the oxidation of the $\text{Mo}_{1.33}\text{CT}_2$ upon adding the Ti$_2$C$_2$T$_6$ MXene.

The SEM cross-section images for the $\text{Mo}_{1.33}\text{CT}_2$ (Fig. 2f), 3Mo:1Ti (Fig. 2g, and Figs. S2f–g), 1Mo:1Ti (Fig. 2h, and Figs. S2h–i), and Ti$_2$C$_2$T$_6$ (Fig. 2) films indicated that the pristine MXene films had a more compact structure than those of the composite films. For notably, the 3Mo:1Ti film shows larger spacing between the MXene layers (i.e., it is more porous) than those of the pristine MXene films. In addition, the composite MXene films showed a slightly curved layer morphology, which can enhance in-plane ion transport and hence increase the number of accessible active sites during electrochemical cycling, as described in earlier reports on modified Ti$_2$C$_2$T$_6$ MXene.[29] This curved layer morphology was observed over a large part of the composite MXene films, as confirmed by SEM images collected from different regions (see Fig. S2f–i). It should be noted that the EDX elemental mapping shows an even distribution of Mo and Ti elements inside the composite films (see Figs. S2h–e), reflecting the film’s homogeneity.

The X-ray diffraction (XRD) patterns for the pristine Ti$_2$C$_2$T$_6$ and $\text{Mo}_{1.33}\text{CT}_2$ showed a typical pattern, with 001 reflections and 0001 reflections, respectively (see Fig. 3c). The 002 peak of the Ti$_2$C$_2$T$_6$ MXene was located at 7.5 (corresponding to a d-spacing of about 11.7 Å), and the $\text{Mo}_{1.33}\text{CT}_2$ 0002 reflection was observed at 5.9 (corresponding to a d-spacing of about 15.0 Å). Notably, the composite films’ low-angle peaks were found at 5.5 and 5.3 (corresponding to a d-spacing of 16.0–16.5 Å). As the content of the $\text{Mo}_{1.33}\text{CT}_2$ MXene increases, the shift toward lower angles increases. The corresponding increase in the d-spacing of the composite films in comparison to the Ti$_2$C$_2$T$_6$ and $\text{Mo}_{1.33}\text{CT}_2$ pristine MXenes suggests that the composite MXene films can host more intercalated ions than the Ti$_2$C$_2$T$_6$ and $\text{Mo}_{1.33}\text{CT}_2$ pristine MXenes, and hence attain a higher capacitance.

Based on the results of XRD, SEM, and conductivity measurements discussed above, the composite films are expected to provide a superior electrochemical performance for supercapacitors and batteries owing to their high electronic conductivity and their morphology of less compact stacking.[29,30] In the following discussions, we provide a general exploration of the electrochemical performance of mixed MXene films. We focus mainly on supercapacitors, but a brief investigation of their performance in lithium-ion batteries is also presented.

**2.2. Electrochemical performance of the composite MXene films in supercapacitors**

**2.2.1. Electrochemical performance on gold/stainless-steel current collectors**

The electrochemical performance of the composite films was studied using a three-electrode stainless-steel Swagelok cell with a gold current collector, see Fig. 4. A stable electrochemical behavior was observed for the composite MXene films when using a potential window of −0.3 ~
cycles at a scan rate of 10 mV s\(^{-1}\) vs. Ag/AgCl [51]. The electrodes were initially precycled for 30 cycles at a scan rate of 10 mV s\(^{-1}\) (see Fig. S5). Only the Ti\(_3\)C\(_2\)T\(_2\) electrodes showed a bit of anodic oxidation during the first CV cycle, which then stabilized in subsequent cycles. As a general trend, the electrode capacitance was raised during the precycling process, as a result of the structure opening up and increasing the interfacial surface area of the electrode accessed by the electrolyte. As can be seen from the CV shapes in Fig. 4a, typical pseudocapacitive CVs were observed for the pristine MXenes and the composite electrodes as well. Likewise, the constant current measurements showed a similar behavior to the CV experiments, with a sloping plateau, see Fig. 4b. The 3Mo:1Ti electrodes delivered discharge capacitances of about 324 and 176 F g\(^{-1}\), at current densities of 3 and 10 A g\(^{-1}\), respectively, while the 1Mo:1Ti electrodes delivered discharge capacitances of about 226 and 142 F g\(^{-1}\), at the same current densities.

The variation of the gravimetric and volumetric capacitances of the composite MXene films with scan rates are shown in Fig. 4c and d. Notably, the composite MXene electrodes featured higher gravimetric and volumetric capacitances than the pristine Ti\(_3\)C\(_2\)T\(_2\) MXenes. The higher capacitance may have originated from a larger space between the MXene sheets in the composite electrodes, as a consequence of the increased iR-drop as a result of their lower electronic conductivity [60]. It should also be noted that both MXenes Mo\(_{1.33}\)CT\(_2\) and Ti\(_3\)C\(_2\)T\(_2\) have mixed surface terminations (T) of F, OH, and O [10,44], and accordingly, the mixed MXene composites most likely maintain similar terminations. Therefore, the surface terminations of the mixed MXene films possibly affect the electrochemical behavior (in H\(_2\)SO\(_4\) solutions) in analogous way to that reported earlier for pristine MXenes [3,4,10,45].

The long-term cycling of the 1Mo:1Ti (see Fig. S6a) and 3Mo:1Ti (see Fig. S6b) electrodes at a current density of about 10 A g\(^{-1}\), showed stable behavior over 10,000 cycles, with a coulombic efficiency approaching 100%. However, the capacitance retentions were about 80% for both composites. One possible reason for the fading is the dissolution of Ti\(_3\)C\(_2\)T\(_2\) upon raising the potential above 0.2 V [61]. Therefore, we performed analogous experiments where the upper cut-off potential was limited to 0.2 V (i.e. a potential window between –0.3 and 0.2 V). Notably, the change in capacitance with scan rate for the 1Mo:1Ti electrode, obtained using an upper cut-off potential of 0.2 V.
was identical to that obtained using an upper cut-off potential of 0.3 V (see Fig. S6c). Furthermore, the fading was successfully reduced, and a capacitance retention of about 96% was obtained after 17,000 cycles for the 1Mo:1Ti electrodes (see Fig. S6e). In comparison, the capacitances of the 3Mo:1Ti electrodes were reduced upon using an upper cut-off potential of 0.2 V (see Fig. S6d), while the capacitance retention was improved in comparison to that using an upper cut-off potential of 0.3 V (see Fig. S6f). The 3Mo:1Ti electrodes showed impressive stability over 27,000 cycles. Furthermore, the morphology of the electrodes was maintained after the long-term cycling (see Fig. S7). The coulombic efficiency was almost 100%, reflecting the high reversibility of the electrochemical cycling. In addition, the increase in capacitance during electrochemical cycling seen in Fig. S6f can be explained by the fact that the composite electrode structure is further opened up during the long-term cycling (see Fig. S7).

2.2.2. Composite MXene films based on Mo$_{1.33}$CT$_z$ prepared from Y-based MAX phase

The abovementioned composite films were obtained using Mo$_{1.33}$CT$_z$ MXene prepared using (Mo$_{2/3}$Y$_{1/3}$)$_2$ALC MAX phase. However, motivated by a comparatively low abundance of Sc, we also investigated alternative pathways. Previous reports have shown that the Mo$_{1.33}$CT$_z$ MXene derived from a Y-based parent i-MAX phase, (Mo$_{2/3}$Y$_{1/3}$)$_2$ALC, behaves similarly to the Mo$_{1.33}$CT$_z$ MXene obtained from a Sc-based MAX phase, (Mo$_{2/3}$Sc$_{1/3}$)$_2$ALC [46,47]. Inspired by the electrochemical performance of this MXene, we analogously synthesized composite films using 75% (weight%) of Mo$_{1.33}$CT$_z$[Y] and 25% of Ti$_3$C$_2$T$_z$. The formed composite film was flexible (see insets in Fig. 5c) and assigned as 3Mo[Y]:1Ti. The SEM cross-section image displayed a typical layered morphology analogous to that of the 3Mo[Sc]:1Ti film (see inset in Fig. 5b). Also, the XRD pattern of the 3Mo[Y]:1Ti film to a great extent matched that of the 3Mo[Sc]:1Ti film (see Fig. 5a). The minor differences between 3Mo[Y]:1Ti and 3Mo[Sc]:1Ti patterns can be attributed to the different degree of stacking/crystallinity of the pristine Mo$_{1.33}$CT$_z$.
MXenes.

The CV shape of the 3Mo[Y]:1Ti electrodes at a scan rate of 10 mV s\(^{-1}\), shown in Fig. 5b, was very similar to that of the 3Mo[Sc]:1Ti, reflecting the fact that the electrochemical behavior of the two films is similar. Likewise, the variation of capacitance with scan rate showed a higher specific capacitance than those of the pristine MXenes, but, analogous to the 3Mo[Sc]:1Ti, with a minor difference in the rate performance (see Fig. 5c). These results clearly indicate that the morphology, structure, and electrochemical performance of the composite MXene films are independent of the origin of the pristine morphology, structure, and electrochemical performance (see Fig. 5c). These results clearly indicate that the electrochemical behavior of the two films is similar. Likewise, the variation of capacitance with scan rate showed a higher specific capacitance than those of the pristine MXenes, but, analogous to the 3Mo[Sc]:1Ti, with a minor difference in the rate performance (see Fig. 5c). These results clearly indicate that the morphology, structure, and electrochemical performance of the composite MXene films are independent of the origin of the pristine MXene. This allows the use of the (Mo\(_{1.33}\))\(_{2}\)AlC i-MAX phase during MXene production.

2.2.3. The electrochemical performance on glassy carbon current collectors

The use of a glassy carbon current collector can expand the potential window of the MXene electrochemical cycling, since the H\(_2\) evolution is suppressed to a more negative potential than with gold/stainless-steel. [62] The electrochemical performance of the composite films was therefore studied using a three-electrode plastic Swagelok cell with glassy carbon current collectors (see Fig. 6). The use of glassy carbon not only enabled the expansion of the potential window (−0.5 ~ 0.2 V vs. Ag/AgCl), but also improved the rate capability of the 1Mo:1Ti electrodes (see Fig. 6b). As can be seen from the CV shapes in Fig. 6a, typical pseudocapacitive CVs were observed for the pristine MXenes and the composite electrodes. However, a couple of redox peaks were observed upon expanding the potential window. These peaks were not detected on a stainless-steel substrate (see Fig. S8) due to the incomplete reduction of the electrodes at the lower cut-off potential (−0.3 V). The peak-to-peak separation increases when going from 1Mo:1Ti to 3Mo:1Ti electrodes, which can be attributed to the increased iR-drop as a result of the lower electronic conductivity of the 3Mo:1Ti electrodes compared to that of the 1Mo:1Ti electrodes. The latter observation explains the good rate performance of the 1Mo:1Ti electrodes compared to 3Mo:1Ti electrodes (see Fig. 6c and d).

As a general trend, the composite MXene electrodes delivered higher gravimetric and volumetric capacitances than the pristine Ti\(_3\)C\(_2\)T\(_2\) (blue circles in Figs. 6c and d) and 3Mo[Sc]C\(_2\)T\(_2\) (purple triangles in Figs. 6c and d) MXenes. As mentioned above, the higher capacitance can be attributed to the presence of more space between the MXene layers of the composite electrodes due to a more curved layer morphology. [29] The 3Mo:1Ti electrodes (red squares in Figs. 6c and d) delivered a high gravimetric (430 F g\(^{-1}\)) and volumetric (1290 F cm\(^{-3}\)) capacitance at a low scan rate (2 mV s\(^{-1}\)), however, the capacitance dropped to 55 F g\(^{-1}\) (165 F cm\(^{-3}\)) and 15 F g\(^{-1}\) (45 F cm\(^{-3}\)) at scan rates of 200 and 1000 mV s\(^{-1}\), respectively. In other words, the capacitance retention was about 13% and 4% at scan rates of 200 and 1000 mV s\(^{-1}\), respectively. In contrast, the 1Mo:1Ti electrodes (black diamonds in Figs. 6c and d) delivered a lower capacitance (304 F g\(^{-1}\)) at a low scan rate (2 mV s\(^{-1}\)), while at scan rates of 200 and 1000 mV s\(^{-1}\) the electrodes delivered capacitances of 165 F g\(^{-1}\) (516 F cm\(^{-3}\)) and 74 F g\(^{-1}\) (230 F cm\(^{-3}\)), respectively. This corresponds to a capacitance retention of about 55% and 25% at scan rates of 200 and 1000 mV s\(^{-1}\), respectively. The long-term cycling of the electrodes was stable over 10,000 cycles, with excellent retention and coulombic efficiency (see
The increase in capacitance during electrochemical cycling matches the results obtained using a stainless-steel cell and, as mentioned above, this can be attributed to the opening up of the structure of the composite electrodes. A test was performed to investigate the reproducibility of the electrochemical results (see Figs. S9b and c). The results revealed that the electrochemical behavior was the same for electrodes obtained from the same mixed MXene film as well as for another film prepared using reproduced pristine MXene batches. This reflects the good homogeneity and reproducibility of the mixed MXene films and the robustness of the synthesis protocol.

A pathway for improving the performance of the MXene electrodes is the use of 3 M H\textsubscript{2}SO\textsubscript{4} rather than 1 M H\textsubscript{2}SO\textsubscript{4}.\[51,62\] Fig. 7a shows a comparison between the CVs at a scan rate 10 mV s\textsuperscript{-1} of the 1Mo:1Ti electrodes in 3 M (black solid line) and 1 M (purple dotted line) H\textsubscript{2}SO\textsubscript{4}. When 3 M H\textsubscript{2}SO\textsubscript{4} electrolyte was used, a significant increase in the capacitance was observed. Furthermore, a promising rate performance was obtained; for instance, at a current density of 20 A g\textsuperscript{-1}, the 1Mo:1Ti electrodes delivered a capacitance of about 282 F g\textsuperscript{-1} (875 F cm\textsuperscript{3}) and 80% of the capacitance was retained after 10,000 cycles with a coulombic efficiency approaching 100% (see Fig. 7c and d). Likewise, the 3Mo:1Ti showed an analogous CV shape to that of 1Mo:1Ti film (see Fig. 7b). In addition, an enhancement of the specific capacitance and rate capability was also obtained. For example, at current densities of about 10 and 100 A g\textsuperscript{-1}, the 3Mo:1Ti electrodes delivered capacitances of about 282 F g\textsuperscript{-1} (875 F cm\textsuperscript{3}) and 864 F cm\textsuperscript{3} (288 F g\textsuperscript{-1}), respectively (see Figs. S10 and S11). However, the capacitance retention was about 85% after 2000 cycles at a high current density of 100 A g\textsuperscript{-1} (see Fig. S11). Therefore, the use of 3 M H\textsubscript{2}SO\textsubscript{4} can enhance the capacitance and rate performance. This can be attributed to the higher conductivity of 3 M as compared to 1 M H\textsubscript{2}SO\textsubscript{4} solutions.\[63\] However, it also reduces the long-term stability as a result of the dissolution of active material in the electrolyte, as well as the presence of parasitic side reactions such as H\textsubscript{2} evolution which is dependent on the concentration of H\textsuperscript{+} in the electrolyte solution.\[64\] The low coulombic efficiency at low rates (not shown) further confirmed the presence of parasitic side reactions. The dissolution of the active materials was also revealed by the change in the electrolyte color after long-term cycling.

Table S5 and Fig. S12 summarize a comparison of the electrochemical performance in supercapacitors for the Mo\textsubscript{1.33}CT\textsubscript{2}z-Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{2}z electrodes reported in this work and the other state-of-the-art for Ti- and Mo-based MXene electrodes. The comparison illustrates the superior performance of the mixed MXene electrodes in terms of high capacitance, good rate performance, and high capacitance retention during long-term cycling.

2.3. Composite MXene films used in asymmetric supercapacitor devices

The 3Mo:1Ti film showed the highest capacitance among the investigated composite MXene films. Therefore, it was chosen as the negative electrode for an asymmetric supercapacitor (ASC) with an activated carbon positive electrode. As shown in Fig. 8a, the composite MXene (3Mo:1Ti) has a working potential window of ~0.5 ~ 0.2 V (vs. Ag/AgCl), whereas the activated carbon has a potential window 0.0 ~ 1.0 V (vs. Ag/AgCl). Therefore, the asymmetric device featured a cell voltage of about 1.5 V. Cyclic voltammetry and constant-current measurements were used to test the electrochemical performance of the ASC.
The device was precycled for 200 cycles at 10 mV s\(^{-1}\) to obtain a stable electrochemical response with a typical pseudocapacitive CV shape (see Figs. 8 b and S13). The ASC delivered discharge capacitances of about 57, 42, and 14 F g\(^{-1}\) at scan rates of 2, 20, and 200 mV s\(^{-1}\), respectively (see Fig. 8b and d). In other words, capacitance retentions of about 74% and 25% were obtained upon increasing the scan rate by a factor of 10 and 100, respectively, reflecting the good rate performance of the ASC. Likewise, the constant current measurements showed sloping charge/discharge profiles, with discharge capacitances of about 50 and 10 F g\(^{-1}\) at current densities of about 0.5 and 5 A g\(^{-1}\), respectively (see Fig. 8c and d). The device featured an energy density of about 16–18 Wh kg\(^{-1}\), and a good capacitance retention (~75%) after long-term cycling at 5 A g\(^{-1}\).

### 2.4. Composite MXene films used in lithium-ion batteries

Inspired by the superior performance of the composite MXene film (3Mo:1Ti) in supercapacitors, we tested it as a negative electrode material for a Li-ion battery. Cyclic voltammetry and galvanostatic charge-discharge techniques were used to examine the electrochemical behavior for lithiation/delithiation in the potential window 0.05 ~ 3.0 V vs. Li\(^+/\)Li. The electrodes were first cycled at 5 mV s\(^{-1}\) for about 200 cycles to obtain a steady-state electrochemical performance. The capacity of the electrodes increased during this precycling (see Fig. S14a), indicating an increase in the interfacial surface area accessed by the electrolyte as a result of the structure opening up upon electrochemical cycling. Analogous behavior was previously observed for Mo\(_2\)CT\(_2\) MXene [65]. The CVs showed a pseudocapacitive CV shape with a redox pair at potentials of 0.8 and 1.4 V (vs. Li\(^+/\)Li), in agreement with previous reports on molybdenum based MXenes [53,65]. Anasori et. al. showed that the electrochemical lithiation mechanism of molybdenum based MXenes can be described as adsorption/intercalation of Li-ions up to a lower cut-off potential \(\geq 1.6\) V (vs. Li\(^+/\)Li), and a conversion reaction below 0.6 V (vs. Li\(^+/\)Li) [53]. Considering our lower cut-off potential of 0.05 V (vs. Li\(^+/\)Li), we possibly have both lithiation mechanisms. The CV rate performance (see Figs. S14b–d) showed capacities of about 106, 81, 46, 36, 24, and 15 mAh g\(^{-1}\) at scan rates of 0.05, 0.1, 0.5, 1, 5, and 50 mV s\(^{-1}\), respectively. Likewise, the composite MXene electrodes delivered capacities of about 80, 51, 24, 19, and 13 mAh g\(^{-1}\), at current densities of about 10, 20, 100, 200, and 1000 mA g\(^{-1}\), respectively (see Figs. S15a–c). Furthermore, the low-rate capacity was maintained after cycling at a high rate (see Fig. S15b). In addition, the composite MXene films showed a capacity retention of about 89% after about 400 cycles at a current density of 200 mA g\(^{-1}\). Previous studies showed that the Li-ions adsorption on O termination is more favorable [66] than that on OH and F terminations which can significantly affect the accessible capacity. [67–69] For example the theoretical capacity of O terminated and OH terminated Mo\(_2\)TiC\(_2\) were 181 and 43 mAh g\(^{-1}\), respectively [53]. Providing that the Mo\(_2\)CT\(_2\) has less favorable O terminations and instead possess mixed terminations with a higher F content (proposed formula Mo\(_2\)CO\(_2\)(OH)\(_6\)F\(_{11}\)) [44] which is not favorable for Li-ions adsorption [67–69], the accessible capacity of Mo\(_2\)CT\(_2\) MXene is expected to be lower than that of other molybdenum based MXenes with more favorable O terminations (e.g. Mo\(_2\)CT\(_2\)) [44]. It should also be noted that the accessible capacity of the MXene-based electrodes can be significantly influenced by the method of electrode manufacturing [37], and it has been shown that vacuum-dried MXene electrodes can possess a
lower capacity than those prepared by natural sedimentation [38] or freeze drying [70]. Therefore, future studies on the composite MXene electrodes are recommended, to explore the potential for improvements in the accessible capacity for Li-ion intercalation by modifying the pathways for electrode manufacturing.

Altogether, the mixed MXene approach, comprising the formation of composites with double transition metals (Mo and Ti), enabled improvement in the properties of each individual MXene. According to the mixing ratios, the electronic conductivities of the mixed MXene films were 24–140 times higher than that of Mo$_{1.33}$CTz$_2$ MXene, and the gravimetric capacitances of the mixed MXene films were 1.3–1.9 higher than that of Ti$_3$C$_2$T$_2$. Moreover, the specific capacitance of mixed MXene outperformed the previously reported values for double transition metal MXene (Mo$_2$TiC$_2$Tz) [53]. Future studies are motivated to explore other MXene composites, targeting optimized properties for superior performance in energy storage applications.

3. Conclusion

In summary, we reported a one-step protocol for fabricating composite MXene films based on Ti$_3$C$_2$T$_2$ and Mo$_{1.33}$CTz$_2$ MXenes. The results were independent on the parent material used for derivation of the Mo$_{1.33}$CTz$_2$ MXene, (Mo$_{2.5}$Y$_{1.1}$)$_2$AlC or (Mo$_{2.5}$Sc$_{1.1}$)$_2$AlC i-MAX phase. The composite films were extremely flexible and showed good electronic conductivity (140 S cm$^{-1}$). The SEM cross-section showed that the composite film is more porous and possesses a more curved layer morphology, which may enhance the in-plane ion transport and increase the number of accessible active sites for electrochemical reactions. Furthermore, the EDX elemental mapping showed a homogeneous distribution of Mo and Ti elements within the films.

The composite films featured a high gravimetric and volumetric capacitance in comparison to the pristine MXene films. At a low scan rate, the 3Mo:1Ti film showed a higher capacitance than the 1Mo:1Ti, whereas the performance of the 1Mo:1Ti film was superior to that of 3Mo:1Ti at a high scan rate. This can be attributed to an about 6 times higher electronic conductivity in the former film (1Mo:1Ti). A good capacitance retention was observed for the 1Mo:1Ti and 3Mo:1Ti films, 96% and 109% after more than 17,000 and 27,000 cycles, respectively. The use of a glassy carbon current collector can expand the potential window of cycling (−0.5 ~ 0.2 V vs. Ag/AgCl), compared to (−0.3 ~ 0.2 V vs. Ag/AgCl) on gold/stainless steel. The use of 3 M H$_2$SO$_4$ improved both the capacitance and the rate performance; however, it reduced the reversibility at low rates due to parasitic side reactions. Furthermore, an asymmetric supercapacitor (ASC) of a composite MXene film and activated carbon featured an operating potential of 1.5 V, a capacitance of about 57 F g$^{-1}$, and an energy density of about 16–18 Wh kg$^{-1}$. The composite MXene was also tested as a negative electrode for a lithium-ion battery, delivering a capacity of about 106 mAh g$^{-1}$.

4. Experimental

4.1. Synthesis of Mo$_{1.33}$CTz$_2$ MXene and -Ti$_3$C$_2$T$_2$ MXenes

4.1.1. Synthesis of Ti$_3$C$_2$T$_2$ (MXene)

To produce Ti$_3$C$_2$T$_2$ (MXene), first the Ti$_3$AlC$_2$ precursor had to be
synthesized. Powders of Ti$_3$AlC$_2$ were produced, starting with a mixture of TiC (Alfa Aesar, 98+ %), Ti (Alfa Aesar, 98+ %) and Al (Alfa Aesar, 98+ %) in a 1:1:2 molar ratio, which were mixed together using a mortar and pestle for 5 min. They were then inserted into an aluminium tube furnace with Ar gas flowing. The furnace was heated at a rate of 5 °C/min up to 1450 °C and held for 280 min, then cooled down to room temperature. The resulting material is a lightly sintered Ti$_3$AlC$_2$ sample, which is then ground into a powder of particle size < 60 μm using a mortar and pestle (see Fig. S1).

To convert the Ti$_3$AlC$_2$ to Ti$_3$C$_2$T$_2$ flakes, half a gram of Ti$_3$AlC$_2$ powder was added to a premixed 10 ml aqueous solution of 12 M HCl (Fisher, technical grade) and 2.3 M LiF (Alfa Aesar, 98+ %) in a Teflon bottle. Prior to adding the MAX powder to the HCl-LiF solution, the latter was placed in an ice bath. After adding the MAX powder, the whole mixture was heated in the ice bath for 0.5 h to avoid the initial overheating that can result from the exothermic nature of the reaction. The bottle was then placed on a magnetic stirrer hot plate in an oil bath and held at 35 °C for 24 h, after which the mixture was washed through 3 cycles of 40 ml of 1 M HCl, followed by 3 cycles of 40 ml of 1 M LiCl (Alfa Aesar, 98+ %). Then, the mixture was washed through repeated cycles of 40 ml of distilled water until the supernatant reached a pH of approximately 6. After washing, 45 ml of distilled water were added and deaerated by bubbling N$_2$ gas through it. It was then sonicated using an ultrasonic bath for 1 h. The resulting suspension was centrifuged for 20 min at 2000 rpm. The supernatant produced was of a concentration of 4–7.5 mg ml$^{-1}$. More details can be found in Ref. [10].

4.1.2. Synthesis of Mo$_{2/3}$CT$_2$ (MXene) from (Mo$_2$/Sc$_{1/3}$)AlC

The (Mo$_2$/Sc$_{1/3}$)AlC, precursor of Mo$_{2/3}$CT$_2$, was synthesized as described in Ref.[45], using a solid-state reaction of elemental powders of Mo (~3 to 7 μm, Alfa Aesar, Kandel, Germany, 99.999 wt% purity), Sc (99.99%, Standford Advanced Material, USA), Al (99.5%, 325 mesh, Alfa Aesar, Kandel, Germany) and C (99.9995%, 200 mesh, Alfa Aesar, Karlsruhe, Germany) in a 4/3:2/3:1 molar ratio, respectively and manually mixed using a mortar and pestle. The mixture was heated at a rate of 5 °C/min to 1400 °C in an alumina crucible under Ar flow and held at 1500 °C for 2.0 h. After furnace cooling, the lightly sintered sample was crushed, using an agate mortar and pestle, and sieved through a 450-mesh sieve (see Fig. S1)

To produce Mo$_{2/3}$CT$_2$, one gram of the (Mo$_2$/Sc$_{1/3}$)AlC i-MAX phase powder was added to 20 ml 48% HF, stirring for 24 h at room temperature. After the reaction, the product was washed with deionized water. After washing, the multilayer MXene was delaminated into single- or few-layer MXene by intercalating with 10 ml of a solution of 54–56 wt% tetrabutylammonium hydroxide, TBAOH, (Sigma Aldrich, St Louis, USA), and manually mixed using a mortar and pestle. The mixture was heated at a rate of 5 °C/min to 1400 °C in an alumina crucible under Ar flow and held at 1500 °C for 2.0 h. After furnace cooling, the lightly sintered sample was crushed, using an agate mortar and pestle, and sieved through a 450-mesh sieve (see Fig. S1).

To produce Mo$_{2/3}$CT$_2$, one gram of the (Mo$_2$/Sc$_{1/3}$)AlC i-MAX phase powder was added to 20 ml 48% HF, stirring for 24 h at room temperature. After the reaction, the product was washed with deionized water. After washing, the multilayer MXene was delaminated into single- or few-layer MXene by intercalating with 10 ml of a solution of 54–56 wt% tetrabutylammonium hydroxide, TBAOH, (Sigma Aldrich, St Louis, USA), which was shaken manually for 5 min. Extra TBAOH was removed by centrifuging at 5000 rpm for 5 min and by carefully rinsing (three times) with water. Then, water was added to the intercalated powder and the mixture was shaken for 5 min, for delamination into single- or few-layered MXene. Finally, homogeneous delaminated Mo$_{2/3}$CT$_2$ MXene was obtained by centrifuging for 30 min at 3500 rpm with a concentration of 1–2 mg ml$^{-1}$.

4.1.3. Synthesis of Mo$_{2/3}$CT$_2$ (MXene) from (Mo$_2$/Y$_{1/3}$)AlC

The (Mo$_2$/Y$_{1/3}$)AlC, precursor of Mo$_{2/3}$CT$_2$, was synthesized as described in Ref. [46], the Mo (~3 to 7 μm, Alfa Aesar, Kandel, Germany, 99.999 wt% purity), YAl$_8$ (99.4 wt% purity), Al (99.99%, Standford Advanced Material, USA), Al (99.5%, 325 mesh, Plansee Composite Materials, Lechbruck, Germany, 99.4 wt% purity), Al (325 mesh, Alfa Aesar, Kandel, Germany, 99.5 wt% purity), and graphite (~200 mesh, Alfa Aesar, Karlsruhe, Germany, 99.9995 wt% purity) were mixed in the molar ratio of 1.33:1:2.45:1, respectively, corresponding to a stoichiometry of (Mo$_2$/Y$_{1/3}$)AlC. It was then cold pressed into disks 0.5 cm in diameter and 1 mm thick using a manual hydraulic press with pressure of 70 KPa. Afterwards, the cold pressed samples were placed in an alumina crucible and inserted into a horizontal tube furnace. The furnace was heated, under a 5 sccm Ar flow, at 5 °C/min to 1500 °C and was held at that temperature for 10 h. After furnace cooling, the samples were crushed once again, using a mortar and pestle, and sieved through a 450-mesh sieve.

Two grams of (Mo$_2$/Y$_{1/3}$)AlC(Aly) powders (~450 mesh) were immersed in a Teflon bottle containing 40 ml of 25 vol% HF (Sigma Aldrich, St. Louis, USA). The mixture was stirred using a Teflon-coated magnetic stirrer bar for 120 h at RT. The resulting mixture was washed with N$_2$ deaerated deionized (DI) water for several cycles until the pH was ≈ 6 (typically, 8 cycles were needed). For each washing cycle, 40 ml of DI water were added to the multilayer powder in a centrifuge tube, which was hand-shaken for 1 min, then centrifuged at 5000 rpm for 1 min, after which the supernatant was decanted. For delamination, 1 g of the multilayer powder was added to 5 ml of an aqueous solution of 54–56 wt% TBAOH. The mixture was hand-shaken for 5 min, and then washed 3 times, using 40 ml deaerated DI water each time. Subsequently, 50 ml of deaerated DI water was added to the intercalated powder and hand-shaken for 5 min, followed by centrifuging at 2500 rpm for 30 min. The resultant supernatant contained delaminated single- or few-layer Mo$_{2/3}$CT$_2$ flakes at a concentration of 3 mg ml$^{-1}$.

4.2. Synthesis of composite MXene films

The prepared MXene suspensions were mixed according to the weight ratios summarized in Table 1, and then shaken by hand for 30 s, followed by vacuum filtration using a Celgard 3501 membrane. The films were allowed to dry in air, peeled off the Celgard membrane, and stored under inert Ar atmosphere for further use.

4.3. Material characterization and electrochemical measurements

A scanning electron microscope (SEM, LEO 1550 Gemini) mounted with an energy-dispersive X-ray (EDX) detector was used to explore the morphology, thickness, and homogeneity of the composite MXene films. X-ray diffraction (XRD) patterns were collected using a PANalytical d diffractometer equipped with Cu K$_\alpha$ radiation source ($\lambda$ = 1.54 Å, step size 0.0084, time per step 20 s).

X-ray photoelectron spectroscopy (XPS) measurements were performed on freestanding film samples of Mo$_{3/3}$CT$_3$, 3Mo1Ti, 1Mo3Ti, 1Mo:3Ti, and Ti$_2$C$_2$T$_2$ using a surface analysis system (Kratos AXIS UltraDLD, Manchester, UK) with monochromatic Al-K$_\alpha$ (1486.6 eV) radiation. The sample was mounted on double-sided tape and grounded to the sample stage with copper contacts. The X-ray beam irradiated the sample surface at an angle of 45° with respect to the surface and provided an X-ray spot of ~300 × 800 μm. Charge neutralization was performed using a co-axial, low energy (~0.1 eV) electron flood source to avoid shifts in the recorded binding energy (BE). XPS spectra were recorded for Ti 2p, Mo 3d, and C 1s regions. The analyzer pass energy used for all regions was 20 eV, with a step size of 0.1 eV. The BE scale of all the XPS spectra was referenced to the Fermi-edge (E$_F$), which was set to a BE of zero eV. The peak fitting was carried out using CasaXPS Version 2.3.16 RP 1.6 in the same manner as in Refs [65,71]. The XPS survey spectra were used to obtain the global atomic elemental percentage. For that measurement, the analyzer pass energy was set to 160 eV and the step size was 0.1 eV.

All electrochemical analysis was done using three-electrode stainless-steel and plastic Swagelok cells with gold and glassy carbon current collectors, respectively. A piece of Celgard 3501 soaked in 1 M or 3 M H$_2$SO$_4$ solution was used as the separator. An Ag/AgCl (3.5 M KCl) and a circular piece of activated carbon (YP-50, Kuraray, Japan) were employed as the reference and counter electrodes, respectively. The pristine MXene and composite MXene films were used as the working electrodes. These working electrodes had a diameter of about 4.0 mm and their overall mass varied between 250 and 270 μg. Cyclic voltammetry and constant-current techniques were used to explore the electrochemical activity of the electrodes. For the measurements using gold/
stainless-steel cells, potential windows of 0.3 – 0.3 V vs. Ag/AgCl or –0.3 ~ 0.2 V, were used. Whereas a potential window of 0.5 – 0.2 V was used for the measurements made using glassy carbon/plastic cells. The packing density of the films was calculated from their areal mass loading and their thickness.

The ASC experiments were carried out using an activated carbon positive electrode and a composite MXene film negative electrode. The electrodes’ diameter was 4 mm and their masses (m+ and m−) were balanced according to the equivalent stored charge (Q+= Q−) using the equation (Q+/Q− = specific capacitance * m+/m−). Cyclic voltammetry and galvanostatic charge-discharge techniques were employed to examine the electrochemical behavior of the ASC devices, and the cell voltage was varied between 0 and 1.5 V. The energy density (E) was calculated using the equation (E (Wh kg−1) = 0.5 * specific capacitance (F g−1) × (potential window (V))3 / 36).

The electrochemical performance of composite MXene in a lithium-ion battery was measured using a coin cell with a lithium metal (potential window (V)) was varied between 0 and 1.5 V. The energy density (E) was calculated for the electrochemical behavior of the ASC devices, and the cell voltage was varied between 0 and 1.5 V. The energy density (E) was calculated using the equation (E (Wh kg−1) = 0.5 * specific capacitance (F g−1) × (potential window (V))3 / 36).

The electrochemical performance of composite MXene in a lithium-ion battery was measured using a coin cell with a lithium metal counter electrode and composite MXene working electrode. The cells were assembled in an Ar-filled glove box (O2 levels = 1 ppm). A piece of glass fiber paper was used as a separator and 1 M LiPF6 in a 1:1 mixture of ethylene carbonate (EC): diethyl carbonate (DEC) was used as the electrolyte. Cyclic voltammetry and galvanostatic charging/discharging in the potential window 0.05 ~ 0.3 V vs. Li/Li+ were used to test the lithium-ion cells.

CRediT authorship contribution statement

Ahmed S. Etman: Investigation, Conceptualization, Methodology, Validation, Visualization, Writing - original draft. Joseph Halim: Formal analysis, Visualization, Writing - original draft. Johanna Rosen: Supervision, Validation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at https://doi.org/10.1016/j.nanoen.2019.06.013.
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