Advantage of Larger Interlayer Spacing of a Mo$_2$Ti$_2$C$_3$ MXene Free-Standing Film Electrode toward an Excellent Performance Supercapacitor in a Binary Ionic Liquid–Organic Electrolyte

Dayakar Gandla, Fuming Zhang, and Daniel Q. Tan*

Cite This: ACS Omega 2022, 7, 7190–7198

ACCESS Metrics & More

ABSTRACT: MXenes show outstanding specific capacitance in aqueous electrolytes. However, the narrow potential window of aqueous electrolytes restrains the energy density. Ionic liquid electrolytes can provide a higher potential window and superior specific energy but are subject to slow ion transport and difficult intercalation for their larger ion size. It is desirable to explore larger interlayer-spaced ($d$-spaced) MXenes that can facilitate the large ion intercalation–deintercalation process. This work reports the first-ever supercapacitor application of the Mo$_2$Ti$_2$C$_3$ MXene free-standing film electrode (f-Mo$_2$Ti$_2$C$_3$) using 1 M 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide (EMIMTF-SI) in acetonitrile electrolyte. Without any preintercalating agents, the authors achieved an interlayer spacing of $\sim$2.4 nm in the f-Mo$_2$Ti$_2$C$_3$ material through etching, followed by a vacuum-assisted filtration technique. The microstructure, electrochemical properties, and charge storage kinetics of the f-Mo$_2$Ti$_2$C$_3$ outperform the conventional f-Ti$_3$C$_2$Tx. The f-Mo$_2$Ti$_2$C$_3$-based symmetric two-electrode device exhibited remarkable specific energy and specific power of 188 Wh kg$^{-1}$ and 22 kW kg$^{-1}$, respectively, along with a high specific capacitance of 152 F g$^{-1}$. This larger $d$-spaced f-Mo$_2$Ti$_2$C$_3$ can emerge as a better alternative to the conventional f-Ti$_3$C$_2$Tx in ionic liquid electrolytes to design next-generation high-performance MXene supercapacitors.

1. INTRODUCTION

Electrochemical supercapacitors are the primary energy storage devices and promising alternatives to rechargeable batteries due to their superior cycle life, high power density, and faster charge/discharge rates.$^1$ However, supercapacitors are notorious for their low energy density (<12 Wh kg$^{-1}$), which dramatically limits their widespread applications in portable and hybrid electric devices.$^2$ To alleviate the low energy density issue, it is imperative to discover new electrode materials and engineer them to be compatible with large voltage window electrolytes.$^3$ A supercapacitor of higher energy storage requires an electrode material to possess a large charge accumulation capability for a specified working voltage. On the other hand, it also requires high electrical conductivity to ensure the rapid discharge merit of the device. Therefore, searching for and developing better electrode materials exhibiting higher specific surface area and higher ion accessibility and conductivity is a hot research topic.

MXenes, a new and exciting class of 2D planar structures, have over 70 different compositions predicted theoretically and over 30 different compositions experimentally synthesized thus far.$^7$ These transition metal carbides and/or nitrides, despite being in the early stages of application for energy storage, have been proven to be promising electrode materials for supercapacitors due to their excellent electrical conductivity, hydrophilic behavior, unique layered structure, mechanical strength, and ability to host cations of different sizes.$^5,6$ These atomically thin materials, with a general formula of M$_{n+1}$X$_n$T$_x$, can be obtained by selectively etching A-layers (Al, Ga, etc.) from their ternary layered M$_{n+1}$AX$_n$ phase, leaving a relatively larger interlayer spacing. In MXenes, M is an early transition metal (e.g., Ti, Nb, Mo, Ta, and Zr); X is carbon and/or nitrogen; T$_x$ represents the surface functional groups such as OH, O, and/or F groups; and $n = 1, 2, o r3$. For instance, Ti$_3$C$_2$ has an interlayer spacing of $\sim$0.2 nm, a lattice constant of 0.3104 nm, and a monolayer thickness of 0.4639 nm.$^8$ Yet, the greater potential of MXene electrodes has not been fully demonstrated because most of the MXenes studied for supercapacitors are limited to two-element carbide with...
limited interlayer spacing and thus aqueous electrolytes to accommodate the smaller ionic size. As a result, their advantage of engineering MXene interlayer spacings has not been well utilized. Using larger ions of organic electrolytes (0.65–1.3 nm) or ionic liquids (0.75–1.4 nm) impedes their intercalation and transportation between the layers of MXenes, limiting the specific capacitance and rate capability compared to smaller size aqueous electrolytes. Although potassium-ion intercalation between the MXene sheets expanded the interlayer spacing from 0.2 to 0.77 nm, they are still relatively smaller than the ions of nonaqueous electrolytes. Therefore, research and publications on high performance supercapacitors enabled by MXenes are scarce in organic and ionic liquid electrolytes. For instance, Dall’Agnese et al. reported a specific capacitance of 33 F g\(^{-1}\) for multilayer Ti\(_3\)C\(_2\)T\(_x\) paper in 1 M EMIMTFSI in acetonitrile electrolyte. Lin et al. reported a capacitance of 70 F g\(^{-1}\) using a Ti\(_3\)C\(_2\)T\(_x\) ionogel electrode in a neat EMIMTFSI electrolyte. However, the specific capacitance and specific energy are pretty low due to their smaller interlayer spacing (d-spacing) and limited surface area of the delaminated sheet. This structural factor restricts the intercalation of EMIM\(^+\) ions between the layers. Some work shows the thickness of the Ti\(_3\)C\(_2\) MXene monolayer flake of 2.7 nm and the interlayer spaces between MXene sheets of 1 to 1.5 nm. Although these values are larger than that of 2D graphene, they are still too small for the better intercalation of nonaqueous ions. Hence, it is pivotal to explore larger interlayer-spaced MXenes, which can facilitate the ion intercalation–deintercalation process to achieve high specific capacitance, energy density, and power density.

Recently, density functional theory (DFT) studies predicted that the Mo-based ordered double-transition-metal carbide MXenes, especially Mo\(_2\)Ti\(_2\)C\(_3\), display similar crystal structures, atomic configurations, and morphologies to the layered structures. They possess hexagonal crystal structure and exhibit larger interlayer spacing and extraordinary chemical and electrochemical properties. Kim et al. proved that etching and delamination processing can result in Mo\(_2\)Ti\(_2\)C\(_3\) with interlayer spacing as large as 2.2–4.26 nm, which is the highest maximum space than any other reported MXene materials. Yet, no publications were found on using this feature of MXene for supercapacitors, which motivates our exploration of Mo\(_2\)Ti\(_2\)C\(_3\) in this field. It would be valuable to utilize the larger interlayer spaced MXene as a framework for access to larger ions of ionic liquid electrolyte instead of pre-embedding the interlayer spacing using intercalant agents.

Herein, for the first time, we report the Mo\(_2\)Ti\(_2\)C\(_3\) MXene free-standing film (f-Mo\(_2\)Ti\(_2\)C\(_3\)) for supercapacitor application using 1 M 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) in an acetonitrile electrolyte. Without using any preintercalating agents (stability issue), an interlayer spacing of \(\sim\)2.4 nm is achieved for f-Mo\(_2\)Ti\(_2\)C\(_3\) through etching followed by a vacuum-assisted filtration technique. Compared with f-Ti\(_3\)C\(_2\)Tx, the f-Mo\(_2\)Ti\(_2\)C\(_3\)-based symmetric 2-electrode device exhibits remarkable specific energy and specific power of 188 Wh kg\(^{-1}\) and 22 kW kg\(^{-1}\), respectively, along with a high specific capacitance of 152 F g\(^{-1}\). These values are much superior to the other reported MXene-based electric double-layer supercapacitors and are promising MXenes for supercapacitor application. Their detailed charge storage kinetics was also studied, which is crucial for the further development of MXene-based electrode materials.

### 2. EXPERIMENTAL SECTION

#### 2.1. Synthesis of f-Mo\(_2\)Ti\(_2\)C\(_3\).

The free-standing Mo\(_2\)Ti\(_2\)C\(_3\) MXene film (f-Mo\(_2\)Ti\(_2\)C\(_3\)) was synthesized by selective etching of aluminum layers of Mo\(_2\)Ti\(_2\)AlC\(_3\) (\(\geq\)98%, particle size <44 \(\mu\)m, Laizhou Kai Kai Ceramic Materials Co., Ltd.) followed by delamination. First, 1 g of Mo\(_2\)Ti\(_2\)AlC\(_3\) powder was gradually added to 10 mL of 50% aqueous hydrofluoric acid (HF) solution over a 60 s period. Then, the solution was allowed to stir at 60 °C for 96 h with a speed of 500 rpm. The etchant mixture was washed repeatedly and centrifuged at 3500 rpm for 5 min for each cycle by adding deionized (DI) water until the supernatant reached a pH \(\sim\) 7. The obtained multilayered Mo\(_2\)Ti\(_2\)C\(_3\) sediment was dispersed in DI water under ultrasonication for 2 h and was centrifuged for 1 h at 3500 rpm. The delaminated suspension was filtered using vacuum-assisted filtration through a porous polypropylene (PP) membrane (Celgard, pore size 0.064 \(\mu\)m). The obtained film was peeled off and vacuum-dried at 40 °C for 12 h for further use. For comparative purposes, we have synthesized Ti\(_3\)C\(_2\) MXene film (f-Ti\(_3\)C\(_2\)) through the same method mentioned above using Ti\(_3\)AlC\(_2\) at an etching time of 48 h.

#### 2.2. Characterizations.

The crystallographic structure and phase formation of f-Mo\(_2\)Ti\(_2\)C\(_3\) and f-Ti\(_3\)C\(_2\) were examined using a Smartlab X-ray diffractometer at a scan rate of 6°/min using a 150 mA current, 40 kV voltage, and copper target. The surface elemental composition was evaluated using X-ray photoelectron spectroscopy (XPS) from Thermo Scientific ESCALAB 250Xi, USA, with a monochromer Al K\(\alpha\) as the X-ray source. Transmission electron microscopy (TEM) images were captured on a JEM2100 instrument at an acceleration voltage of 200 kV.

#### 2.3. Electrochemical Performance Testing.

Electrochemical performance tests such as cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), electrochemical impedance spectra (EIS), and galvanostatic cycling were carried out using a Gamry electrochemical workstation (Interface 1010E, USA). The free-standing Mo\(_2\)Ti\(_2\)C\(_3\) films were punched with a diameter of 10 mm and used as cathode and anode electrodes directly without any binders. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI, 1 M) in acetonitrile was used as an electrolyte, and a 35 \(\mu\)m thick cellulose paper (NKK TF4035) having 75% porosity was used as a separator. The two-electrode Swagelok symmetric cells were fabricated and assembled in a glovebox under an argon atmosphere with oxygen and water levels <0.01 ppm. The mass loading at each electrode was \(\sim\)3 mg cm\(^{-2}\). EIS data were recorded with 5 mV amplitude potential within a frequency range of 10 kHz to 0.01 Hz.

The specific capacitance values of the two-electrode cell were calculated using GCD curves from the following equation

\[
C = \frac{I\Delta t}{m\Delta V}
\]

where \(C\) implies the specific capacitance (F g\(^{-1}\)) of the cell; \(I\) represents the discharge current (A); \(\Delta t\) is the discharge time (s); \(m\) is the total mass (g) of active material loaded including cathode and anode; and \(\Delta V\) indicates the potential window (V).

The specific energy (E, Wh kg\(^{-1}\)) and specific power (P, W kg\(^{-1}\)) of the supercapacitor device were calculated using the following equations
\[ E = \frac{C \times \Delta V^2}{2 \times 3.6} \]  
\[ P = \frac{E \times 3600}{\Delta t} \]

where \( C \) indicates the specific capacitance (F g\(^{-1}\)) of the cell; \( \Delta V \) describes the potential window (V); and \( \Delta t \) is the discharge time (s).

3. RESULTS AND DISCUSSION

Figure 1 shows the schematic illustration of the ion intercalation between the layered structure of f-Mo\(_2\)Ti\(_2\)C\(_3\) and f-Ti\(_3\)C\(_2\) with different interlayer spacing. Here the bare ion sizes of EMIM\(^+\) and TFSI\(^-\) are represented (without solvation). The inset shows the photo of a free-standing f-Mo\(_2\)Ti\(_2\)C\(_3\) film.

This phenomenon implies the increase in the interlayer spacing along the c-axis as the Al atoms are replaced by OH, F, and O functional groups, intercalated between the layers. Based on their respective (002) diffraction peaks, the \( d \)-spacing (measured using Bragg’s equation) of f-Mo\(_2\)Ti\(_2\)C\(_3\) and f-Ti\(_3\)C\(_2\) was found to be 2.46 and 1.02 nm, respectively. Such a larger interlayer distance for f-Mo\(_2\)Ti\(_2\)C\(_3\) is indispensable to host the bulky-sized ions from high voltage ionic liquid electrolytes, and this ultimately facilitates the enhanced charge storage capacity.

The surface elemental composition and chemical bonding states of f-Mo\(_2\)Ti\(_2\)C\(_3\) were characterized by X-ray photoelectron spectroscopy (XPS). The XPS survey spectrum of f-Mo\(_2\)Ti\(_2\)C\(_3\) (Figure 2b) confirms the existence of various elements such as Mo, Ti, C, F, and O. As shown in Figure 2c, the high-resolution XPS of Ti 2p was deconvoluted into various subpeaks such as Ti\(^{−}\)C\(_2\)p\(_{3/2}\) at 453.2 eV, Ti\(^{2+}\) at 454.4 eV, Ti\(^{3+}\) at 456.9 eV, Ti\(^{4+}\) at 457.7 eV, Ti\(^{−}\)O\(_2\)p\(_{3/2}\) at 459.7 eV, Ti\(^{−}\)F\(_2\)p\(_{3/2}\) at 462.8 eV, Ti\(^{−}\)O\(_2\)p\(_{1/2}\) at 468.3 eV, Ti\(^{−}\)F\(_2\)p\(_{1/2}\) at 470.3 eV, respectively. Accordingly, the high-resolution XPS of Mo 3d (Figure 2d) was deconvoluted into Mo\(^{−}\)C\(_3\) at 227.5 eV, Mo\(^{4+}\) 3d\(_{5/2}\) at 228.3 eV, Mo\(^{5+}\) 3d\(_{5/2}\) at 230.8 eV, Mo\(^{6+}\) 3d\(_{3/2}\) at 231.3 eV, and Mo\(^{6+}\) 3d\(_{3/2}\) at 234.6 eV, respectively.

Figure 1. Schematic illustration of the ion intercalation between the layered structure of f-Mo\(_2\)Ti\(_2\)C\(_3\) and f-Ti\(_3\)C\(_2\) and a fabricated free-standing film. Using a ball and stick model, one can see that, in f-Mo\(_2\)Ti\(_2\)C\(_3\), the two Ti layers are placed as inner layers and sandwiched between two outer Mo layers. The C atoms are alternatively sandwiched between the Mo and Ti layers at the octahedral sites. Interlayer spacing of 2.4 nm in f-Mo\(_2\)Ti\(_2\)C\(_3\) is large enough for the effective intercalation and distribution of larger sized EMIM\(^+\) and TFSI\(^-\) ions of ionic liquid electrolyte, leading to the higher performance of the supercapacitor compared with the limited access of large ions to the interlayer space in f-Ti\(_3\)C\(_2\) (1.1 nm interlayer spacing). As a result, the large ions in the latter case will primarily access the surface sites and ineffectively intercalate between the layers, resulting in decreased performance.

3.1. Microstructure and Morphological Analysis. XRD analysis was performed to compare the \( d \)-spacing between f-Mo\(_2\)Ti\(_2\)C\(_3\) and f-Ti\(_3\)C\(_2\) and confirm the successful etching and phase formation of f-Mo\(_2\)Ti\(_2\)C\(_3\) from Mo\(_2\)Ti\(_2\)AlC\(_3\) (Figure 2a).

It can be observed that the strongest XRD peak at 2\( \theta \) 41.2\(^°\), corresponding to Mo\(_2\)Ti\(_2\)AlC\(_3\)’s MAX phase, disappeared after etching with the HF solution. Most importantly, the (002) diffraction peak of Mo\(_2\)Ti\(_2\)AlC\(_3\) at 2\( \theta \) 7.6\(^°\) was shifted to a lower angle, i.e., 2\( \theta \) 3.54\(^°\), after the formation of f-Mo\(_2\)Ti\(_2\)C\(_3\). This phenomenon is consistent with the results obtained from the (002) crystal plane of XRD data. The selected area electron diffraction (SAED) spots reveal the polycrystalline nature with hexagonal crystal structure of f-Mo\(_2\)Ti\(_2\)C\(_3\) (Figure 2f), consistent with the previous reports.
3.2. Electrochemical Performance Testing. The advantage of the larger interlayer spacing of the f-Mo$_2$Ti$_2$C$_3$ electrode is anticipated due to the high charge accessibility and transport rate. We studied its electrochemical performance by fabricating a two-electrode symmetric Swagelok cell and using 1 M 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) in an acetonitrile electrolyte. The comparative CV curves of f-Mo$_2$Ti$_2$C$_3$ and f-Ti$_3$C$_2$ at a scan rate of 200 mV s$^{-1}$ are shown in Figure 3a. The CV curves of both electrodes show a slightly distorted quasirectangular shape with partial redox peaks within a potential window of 0–3 V. The current in the CV curve of f-Mo$_2$Ti$_2$C$_3$ was much higher compared to f-Ti$_3$C$_2$, indicating its higher specific capacitance. The high specific capacitance of f-Mo$_2$Ti$_2$C$_3$ can be attributed to its larger interlayer spacing, facilitating better intercalation and accessibility of larger EMIM$^+$ (0.8 nm) ions between the layers rather than adsorbing on the outer layers. The CV curves of f-Mo$_2$Ti$_2$C$_3$ at various scan rates ranging from 5 to 200 mV s$^{-1}$ (Figure 4a) exhibit a similar shape without any deviation, implying its excellent rate capability and reversibility.

The galvanostatic charge–discharge (GCD) curves of f-Mo$_2$Ti$_2$C$_3$ and f-Ti$_3$C$_2$ at a current density of 10 mA cm$^{-2}$ are shown in Figure 3b. The f-Mo$_2$Ti$_2$C$_3$ shows a longer discharge time and a small internal resistance (IR) drop at the beginning of the discharge curves compared to f-Ti$_3$C$_2$. This shows the superior charge storage capacity of f-Mo$_2$Ti$_2$C$_3$ and faster diffusion of EMIM$^+$ and TFSI$^-$ ions at the electrode–
electrolyte interface. The GCD curves of f-Mo$_2$Ti$_2$C$_3$ show a symmetrical triangular shape at various current densities from 10 to 100 mA cm$^{-2}$ (Figure 4b), suggesting its reversible capacitive nature.

The f-Mo$_2$Ti$_2$C$_3$ cell exhibits a much higher specific capacitance of 152$-94$ F g$^{-1}$ compared with the f-Ti$_3$C$_2$ cell of 61$-37$ F g$^{-1}$ at various current densities (Figure 3c), and this is even superior to the previously reported value for MXenes using ionic liquid electrolytes.$^{19,20}$ This higher value is attributed to reversible and better intercalation EMIM$^+$ ions between the layers of larger interlayer spacing of f-Mo$_2$Ti$_2$C$_3$. The lower specific capacitance of f-Ti$_3$C$_2$ can be due to insufficient intercalation of EMIM$^+$ ions. The ions only adhere to the outer surface and inside the narrow interstack space.

The long-term cyclic stability at higher working potential is essential to realize the practical application of MXene-based supercapacitors. The cycle life of f-Mo$_2$Ti$_2$C$_3$ and f-Ti$_3$C$_2$ was studied at a current density of 200 mA cm$^{-2}$. As shown in Figure 3d, the f-Mo$_2$Ti$_2$C$_3$ cell delivers high capacitance retention of 86% after 5000 GCD cycles, whereas f-Ti$_3$C$_2$ shows lower retention of 64% under the same conditions. In addition, f-Mo$_2$Ti$_2$C$_3$ shows a Coulombic efficiency of 98$-100%$, implying its reversible charge$-$discharge behavior. The specific energy and specific power density of the f-Mo$_2$Ti$_2$C$_3$ cell calculated from the specific capacitance using GCD curves are represented in the Ragone plot (Figure 3e). The cell delivers the highest specific energy of 188 W h kg$^{-1}$ (at a specific power of 2.6 kW kg$^{-1}$) and the highest specific power of 22 kW kg$^{-1}$ (at a specific energy of 110 W h kg$^{-1}$). The achieved values are much superior to other MXene-based supercapacitors, carbon-based EDLCs, and hybrid-ion capacitors reported so far.$^{10,21-26}$

Self-discharge is one of the most significant technical issues of the present supercapacitors. To find any reduction in the self-discharge with the expanded interlayer spacing, we measured the open-circuit potentials of the f-Mo$_2$Ti$_2$C$_3$ and f-Ti$_3$C$_2$ cells for 12 h after charging for 1 h at a constant potential of 3 V (Figure 3f). To facilitate this understanding, we divided the decrease in the open-circuit potentials into two parts, the sharp initial decrease followed by the steady-state.
decrease, which were represented by different colors. The f-Ti$_3$C$_2$ showed a large initial voltage drop until 0.5 V from 3 V (pink line), followed by the steady-state decrease (gray line). Contrary to this, the larger interlayer-spaced f-Mo$_2$Ti$_2$C$_3$ showed a 300% decrease in its initial self-discharge behavior. The initial voltage drop was until 1.5 V (purple line), followed by a steady-state decrease (orange line). Most of the charged EMIM$^+$ ions can loosely adhere and quickly diffuse at the outer surface of the f-Ti$_3$C$_2$, which cause a significant loss of ions near the surface, which led to a significant initial potential drop. In the case of f-Mo$_2$Ti$_2$C$_3$, the charged EMIM$^+$ ions can be intercalated between the layers. Due to the confinement effect, the loss of ions from these layers is not so prominent, which causes a minor initial potential drop.\(^1\)

To further investigate the ion transport kinetics and resistance of the f-Mo$_2$Ti$_2$C$_3$ and f-Ti$_3$C$_2$ electrodes in EMIMTFSI electrolyte, electrochemical impedance spectroscopy (EIS) was carried out, and the corresponding Nyquist plot is shown in Figure 4c. The charge transfer resistance ($R_{ct}$) of the f-Mo$_2$Ti$_2$C$_3$ and f-Ti$_3$C$_2$ was measured to be 3.4 Ω and 8.7 Ω, respectively. The smaller $R_{ct}$ of f-Mo$_2$Ti$_2$C$_3$ is attributed to its larger $d$-spacing, which facilitates faster insertion/extraction of bulky EMIM$^+$ and TFSI$^-$ ions between the layers.

### 3.3. Charge Storage Kinetic Studies

In general, the total charge stored in an electrode is contributed from both a surface-controlled capacitive process and diffusion-controlled Faradaic process. The quantitative study of these contributions from CV is a crucial step for a better understanding of the charge storage kinetics in the f-Mo$_2$Ti$_2$C$_3$ electrode. Hence, we analyzed the capacitive and diffusive contributions from the CV data at various scan rates (5–200 mV s$^{-1}$) using the following power-law equation.\(^2\)

\[
i = a \nu^b
\]

The above equation can be written as

\[
\log(i) = \log(a) + b \log(\nu)
\]

where $i$ and $\nu$ are the current (A) and the scan rate (mV s$^{-1}$), and $a$ and $b$ are the adjustable parameters. For a diffusion-controlled process, the current response is proportional to the square root of the scan rate ($b = 0.5$), whereas for a capacitive process, the current response is proportional to the scan rate ($b = 1$). The $b$-values for the f-Mo$_2$Ti$_2$C$_3$ were determined from the slope of the fitted curves between log($i$) vs log($\nu$) in the anodic scan at various potentials. The $b$-values obtained at different potentials were in the range of 0.82–0.93 (Figure 5a), demonstrating both contributions to the total charge storage mechanism and the domination of the surface-controlled capacitive process including an intercalation pseudocapacitive process.\(^2\)

We used the Dunn method to further quantify the capacitive and diffusion-controlled contributions to the whole capacity at a fixed potential at each scan rate.\(^2\)

\[
i(V) = k_1 \nu + k_2 \nu^{1/2}
\]

Here $i(V)$ is the current at a specific potential, and $k_1 \nu$ and $k_2 \nu^{1/2}$ denote the currents from surface-controlled and diffusion-controlled processes, respectively. The above equation can be rearranged as

\[
i(V)/\nu^{1/2} = k_1 \nu^{1/2} + k_2
\]

The $k_1$ and $k_2$ values were derived from the linear plot of $i(V)/\nu^{1/2}$ vs $\nu^{1/2}$ at various scan rates. In this study, the different potentials of 0, 1.5, and 3 V were chosen for the curve fitting (Figure 4d).

The f-Mo$_2$Ti$_2$C$_3$- and f-Ti$_3$C$_2$-based supercapacitors showed a surface-controlled capacitive current of 66% and 38%, respectively.
respectively, at a lower scan rate of 25 mV s$^{-1}$ (Figure 5b and Figure 5c). Upon increasing the scan rate to 200 mV s$^{-1}$, their capacitive contributions increased to 91% and 63%, respectively (Figure 5d and Figure 5e). The high pseudocapacitive current contribution of the f-Mo$_2$Ti$_2$C$_3$ compared to f-Ti$_3$C$_2$ is mainly attributed to its larger interlayer spacing, allowing the free and reversible intercalation/deintercalation of bare and solvated EMIM$^+$ and TFSI$^-$ ions. Here, the pseudocapacitance refers to ‘intercalation pseudocapacitance’, which is quite different from battery-like intercalation. As previously reported, similar to EDLCs, the intercalation pseudocapacitance shows the triangular-shaped GCD curves. The kinetics of the intercalation pseudocapacitance is controlled by the surface process, so the entire behavior is capacitive. In contrast, battery-type intercalation exhibits apparent plateaus in their GCD curves due to crystallographic phase transformation.$^{30}$

In the case of f-Ti$_3$C$_2$, at a lower scan rate, most of the ions reside at the outer surface of the layers, dominating the ion diffusion behavior over capacitive contribution. However, at a high scan rate, the ions partially intercalate/deintercalate between the layers, dominating the intercalation pseudocapacitance over diffusion contribution. The f-Mo$_2$Ti$_2$C$_3$ exhibited a continuous increase in the ratio of capacitive contribution with the increase in the scan rates from 5 to 200 mV s$^{-1}$ (Figure 5f), indicating fast capacitive response at all scan rates, which is beneficial for achieving high power density.$^{3}$

### 4. CONCLUSIONS

In this work, we proved that the f-Mo$_2$Ti$_2$C$_3$ MXene with the larger interlayer spacing (~2.4 nm) is more beneficial than conventional f-Ti$_3$C$_2$ MXene in achieving high specific capacitance, cycle life, and superior specific energy in ionic liquid electrolyte. This phenomenon is attributed to reversible and better intercalation/deintercalation cations between the...
layers of f-Mo2Ti2C3. The self-discharge analysis suggested that, compared to f-Mo2Ti2C3, f-Ti3C2 showed a quick initial potential drop as the charged ions can be loosely bonded and quickly diffused at the outer surface of the f-Ti3C2, which causes significant loss of ions near the surface. According to the charge storage kinetic studies, f-Mo2Ti2C3 exhibits pseudocapacitive-controlled behavior as the dominant charge storage mechanism at all scan rates. On the other hand, f-Ti3C2 shows capacitive-controlled behavior as the dominant charge storage mechanism at all scan rates. This work achieved an excellent specific energy (188 Wh kg⁻¹) and specific power (22 kW kg⁻¹) even without using spacers to enlarge the interlayer spacing of f-Mo2Ti2C3. Therefore, it is feasible to achieve the highest performance using MXene electrode materials on par with the Li-ion batteries in the ionic liquid electrolytes by engineering and optimizing their d-spacing.

■ AUTHOR INFORMATION

Corresponding Author

Daniel Q. Tan — Department of Materials Science and Engineering, Guangdong Technion - Israel Institute of Technology, Shantou, Guangdong S15063, P.R. China; Guangdong Provincial Key Laboratory of Materials and Technologies for Energy Conversion, Guangdong Technion - Israel Institute of Technology, Shantou, Guangdong S15063, P.R. China; orcid.org/0000-0002-2282-2000; Email: daniel.tan@tiit.edu.cn

Authors

Dayakar Gandla — Department of Materials Science and Engineering, Guangdong Technion - Israel Institute of Technology, Shantou, Guangdong S15063, P.R. China; Guangdong Provincial Key Laboratory of Materials and Technologies for Energy Conversion, Guangdong Technion - Israel Institute of Technology, Shantou, Guangdong S15063, P.R. China

Fuming Zhang — Department of Materials Science and Engineering, Guangdong Technion - Israel Institute of Technology, Shantou, Guangdong S15063, P.R. China; Technion Israel Institute of Technology, Haifa 3200003, Israel

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c06761

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by a 2020 Li Ka Shing Foundation Cross-Disciplinary Research grant 2020LKSFG01A, the Guangdong-Israel Special Research grant 200902154890781, and Guangdong Major Project of Basic and Applied Basic Research and 212019071820400001 (Basic and Applied Research of Future functional materials under extreme conditions). Dr. Guanghui Song’s help with sample handling for characterization is appreciated.

■ REFERENCES

(1) Wang, Z.; Xu, Z.; Huang, H.; Chu, X.; Xie, Y.; Xiong, D.; Yan, C.; Zhao, H.; Zhang, H.; Yang, W. Unraveling and Regulating Self-Discharge Behavior of TiC2Tx MXene-Based Supercapacitors. ACS Nano 2020, 14, 4916–4924.

(2) Cheng, W.; Fu, J.; Hu, H.; Ho, D. Interlayer Structure Engineering of MXene-Based Capacitor-Type Electrode for Hybrid Micro-Supercapacitor toward Battery-Level Energy Density. Adv. Sci. 2021, 8, 2100775.

(3) Simon, P.; Gogotsi, Y. Perspectives for Electrochemical Capacitors and Related Devices. Nat. Mater. 2020, 19, 1151–1163.

(4) Han, M.; Shuck, C. E.; Rahmanov, R.; Parchment, D.; Anasori, B.; Koo, C. M.; Friedman, G.; Gogotsi, Y. Beyond Ti3C2Tx: MXenes for Electromagnetic Interference Shielding. ACS Nano 2020, 14, 5008–5016.

(5) Maalal, O.; Naguib, M.; Mochalin, V. N.; Dall’Agne, Y.; Heon, M.; Barsoum, M. W.; Gogotsi, Y. Intercalation and Delamination of Layered Carbides and Carbonitrides. Nat. Commun. 2013, 4, 1–7.

(6) Lukatskaya, M. R.; Maalal, O.; Ren, C. E.; Dall’Agne, Y.; Rozier, P.; Taberna, P.-L.; Naguib, M.; Simon, P.; Barsoum, M. W.; Gogotsi, Y. Cation Intercalation and High Volumetric Capacitance of Two-Dimensional Titanium Carbide. science 2013, 341, 1502–1505.

(7) Anasori, B.; Lukatskaya, M. R.; Gogotsi, Y. 2D Metal Carbides and Nitrides (MXenes) for Energy Storage. Nat. Rev. Mater. 2017, 2, 1–17.

(8) Yorulmaz, U.; Demiroğlu, I.; Çakır, D.; Gülseren, O.; Sevick, C. A Systematical Ab-Initio Review of Promising 2D MXene Monolayers towards Li-Ion Battery Applications. J. Phys. Energy 2020, 2, 032006.

(9) Liang, K.; Matsumoto, R. A.; Zhao, W.; Osti, N. C.; Popov, I.; Thapaliya, B. P.; Fleischmann, S.; Misra, S.; Prenger, K.; Tyagi, M.; Mamontov, E.; Augustyn, V.; Unocic, R. R.; Sokolov, A. P.; Dai, S.; Cummings, P. T.; Naguib, M. Engineering the Interlayer Spacing by Pre-Intercalation for High Performance Supercapacitor MXene Electrodes in Room Temperature Ionic Liquid. Adv. Funct. Mater. 2021, 31, 2107246.

(10) Dall’Agne, Y.; Rozier, P.; Taberna, P.-L.; Gogotsi, Y.; Simon, P. Capacitance of Two-Dimensional Titanium Carbide (MXene) and MXene/Carbon Nanotube Composites in Organic Electrolytes. J. Power Sources 2016, 306, S10.

(11) Lin, Z.; Rozier, P.; Dployer, B.; Taberna, P.-L.; Anasori, B.; Gogotsi, Y.; Simon, P. Electrochemical and In-Situ X-Ray Diffraction Studies of TiC3Tx MXene in Ionic Liquid Electrolyte. Electrochem. Commun. 2016, 72, 50–53.

(12) Pang, J.; Mendes, R. G.; Bachmatiuk, A.; Zhao, L.; Ta, H. Q.; Gemming, T.; Liu, H.; Liu, Z.; Rummeli, M. H. Applications of 2D MXenes in Energy Conversion and Storage Systems. Chem. Soc. Rev. 2015, 44, 72–133.

(13) Anasori, B.; Xie, Y.; Beidaghi, M.; Lu, J.; Hsler, B. C.; Hultman, L.; Kent, P. R. C.; Gogotsi, Y.; Barsoum, M. W. Two-Dimensional, Ordered, Double Transition Metals Carbides (MXenes). ACS Nano 2015, 9, 9507–9516.

(14) Kim, H.; Anasori, B.; Shalkey, H. N. Thermoelectric Properties of Two-Dimensional Molybdenum-Based MXenes. Chem. Mater. 2017, 29, 6472–6479.

(15) Anasori, B.; Shi, C.; Moon, E. J.; Xie, Y.; Voigt, C. A.; Kent, P. R. C.; May, S. J.; Billinge, S. J. L.; Barsoum, M. W.; Gogotsi, Y. Control of Electronic Properties of 2D Carbides (MXenes) by Manipulating Their Transition Metal Layers. Nanoscale Horizons 2016, 1, 227–234.

(16) Anasori, B.; Dahlqvist, M.; Halim, J.; Moon, E. J.; Lu, J.; Hosler, B. C.; Caspi, E. N.; May, S. J.; Hultman, L.; Ekldun, P.; Rosén, J.; Barsoum, M. W. Experimental and Theoretical Characterization of Ordered MAX Phases Mo2TiAlC2 and Mo2Ti2AlC3. J. Appl. Phys. 2015, 118, 094304.

(17) Mendes, R. G.; Ta, H. Q.; Yang, X.; Li, W.; Bachmatiuk, A.; Choi, J.-H.; Gemming, T.; Anasori, B.; Lijun, L.; Fu, L.; Liu, Z.; Rümmeli, M. H. In Situ N-Doped Graphene and Mo Nanoribbon Formation from Mo2TiC3 MXene Monolayers. Small 2020, 16, 1907115.

(18) Futamura, R.; Iiyama, T.; Takasaki, Y.; Gogotsi, Y.; Biggs, M. J.; Salanne, M.; Ségalini, J.; Simon, P.; Kaneko, K. Partial Breaking of the Coulombic Ordering of Ionic Liquids Confined in Carbon Nanopores. Nat. Mater. 2017, 16, 1225–1232.
(19) Lin, Z.; Barbara, D.; Taberna, P. L.; Van Aken, K. L.; Anasori, B.; Gogotsi, Y.; Simon, P. Capacitance of Ti3C2Tx MXene in Ionic Liquid Electrolyte. J. Power Sources 2016, 326, 575−579.

(20) Zheng, S.; Zhang, C.; Zhou, F.; Dong, Y.; Shi, X.; Nicolosi, V.; Wu, Z.-S.; Bao, X. Ionic Liquid Pre-Intercalated MXene Films for Ionogel-Based Flexible Micro-Supercapacitors with High Volumetric Energy Density. J. Mater. Chem. A 2019, 7, 9478−9485.

(21) He, X.; Bi, T.; Zheng, X.; Zhu, W.; Jiang, J. Nickel Cobalt Sulfide Nanoparticles Grown on Titanium Carbide MXenes for High-Performance Supercapacitor. Electrochim. Acta 2020, 332, 135514.

(22) Wang, Y.; Wang, X.; Li, L.; Liu, R.; Bai, Y.; Xiao, H.; Liu, Y.; Yuan, G. Intercalating Ultrathin MoO3 Nanobelts into MXene Film with Ultrahigh Volumetric Capacitance and Excellent Deformation for High-Energy-Density Devices. Nano-Micro Lett. 2020, 12, 115.

(23) Pan, Z.; Cao, F.; Hu, X.; Ji, X. A facile method for synthesizing CuS decorated Ti3C2 MXene with enhanced performance for asymmetric supercapacitors. J. Mater. Chem. A 2019, 7, 8984.

(24) Li, J.; Yang, Q.-Q.; Hu, Y.-X.; Liu, M.-C.; Lu, C.; Zhang, H.; Kong, L.-B.; Liu, W.-W.; Niu, W.-J.; Zhao, K.; Wang, Y.-C.; Cheng, F.; Wang, Z. M.; Chueh, Y.-L. Design of Lamellar Mo2C Nanosheets Assembled by Mo2C Nanoparticles as an Anode Material toward Excellent Sodium-Ion Capacitors. ACS Sustain. Chem. Eng. 2019, 7, 18375−18383.

(25) Xiao, J.; Wen, J.; Zhao, J.; Ma, X.; Gao, H.; Zhang, X. A Safe Etching Route to Synthesize Highly Crystalline Nb2CTx MXene for High Performance Asymmetric Supercapacitor Applications. Electrochim. Acta 2020, 337, 135803.

(26) Wu, W.; Wang, C.; Zhao, C.; Wei, D.; Zhu, J.; Xu, Y. Facile Strategy of Hollow Polyaniline Nanotubes Supported on Ti3C2 MXene Nanosheets for High-Performance Symmetric Supercapacitors. J. Colloid Interface Sci. 2020, 580, 601−613.

(27) Augustyn, V.; Come, J.; Lowe, M. A.; Kim, J. W.; Taberna, P.-L.; Tolbert, S. H.; Abrúña, H. D.; Simon, P.; Dunn, B. High-Rate Electrochemical Energy Storage through Li+ Intercalation Pseudocapacitance. Nat. Mater. 2013, 12, 518−522.

(28) Wang, X.; Mathis, T. S.; Li, K.; Lin, Z.; Vlcek, L.; Torita, T.; Osti, N. C.; Hatter, C.; Urbankowski, P.; Sarycheva, A.; Tyagi, M.; Mamontov, E.; Simon, P.; Gogotsi, Y. Influences from Solvents on Charge Storage in Titanium Carbide MXenes. Nat. Energy 2019, 4, 241−248.

(29) Brezesinski, T.; Wang, J.; Tolbert, S. H.; Dunn, B. Ordered Mesoporous α-MoO3 with Iso-Oriented Nanocrystalline Walls for Thin-Film Pseudocapacitors. Nat. Mater. 2010, 9, 146−151.

(30) Liu, Y.; Jiang, S. P.; Shao, Z. Intercalation pseudocapacitance in electrochemical energy storage: recent advances in fundamental understanding and materials development. Mater. Today Adv. 2020, 7, 100072.