Review

Research Progress on MXene-Based Flexible Supercapacitors: A Review

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Abstract: The increasing demands for portable, intelligent, and wearable electronics have significantly promoted the development of flexible supercapacitors (SCs) with features such as a long lifespan, a high degree of flexibility, and safety. MXenes, a class of unique two-dimensional materials with excellent physical and chemical properties, have been extensively studied as electrode materials for SCs. However, there is little literature that systematically summarizes MXene-based flexible SCs according to different flexible electrode construction methods. Recent progress in flexible electrode fabrication and its application to SCs is reviewed according to different flexible electrode construction methods based on MXenes and their composite electrodes, with or without substrate support. The fabrication methods of flexible electrodes, electrochemical performance, and the related influencing factors of MXene-based flexible SCs are summarized and discussed in detail. In addition, the future possibilities of flexible SCs based on MXene are explored and presented.

Keywords: MXenes; two-dimensional materials; flexible electrode; flexible supercapacitors

1. Introduction

With the emergence of more foldable, wearable, and flexible electronic devices, it is imperative to develop high-performing, safe, and cost-effective flexible energy storage devices that are compact and flexible enough to match these electronic components [1,2]. Due to the benefits of supercapacitors (SCs), such as long cycling, fast charging–discharging rates, and higher power density [3,4], flexible SCs are seen as advantageous candidates for powering flexible devices due to their being space efficient, lightweight, easy to handle, reliable, and compatible with other flexible electronic components [5–7]. They are usually made with thin-film electrode materials in the shape of fibers or flat sheets, with or without soft-matter substrates for support. Active materials are firmly integrated with flexible substrates, which allows the device to be robust and flexible mechanically. Free-standing films, fibers, or papers can serve as flexible electrodes generally without the need for current collectors and insulating binders, providing superior volumetric and gravimetric capacitance. Additionally, they can be easily fabricated into any desired shape or structural form [8]. Many nanostructured materials are frequently used in flexible SCs as electrode materials with improved performance, including carbon nanotubes, hierarchically porous carbon, and hollow metal oxides/sulfides [9–16]. However, there are few electrode materials that can have both high volumetric and gravimetric specific capacitance.

MXenes, a specific class of 2D transition metal carbides and nitrides, are obtained by selectively etching the A layer in their precursor MAX phase, where A is mainly group-13 or group-14 elements [17,18]. Since Ti3C2Tx nanosheets were successfully synthesized with a selective etching method in 2011, MXenes have attracted great attention from scientists [19].
In the past decade, although more than thirty MXenes have been synthesized, including Ti$_2$C$_x$, Ti$_2$NT$_x$, Ti$_2$C$_2$F$_x$, Ti$_4$N$_3$T$_x$, Mo$_2$33CT$_x$, Mo$_2$CT$_x$, Nb$_2$CT$_x$, Nb$_3$C$_3$T$_x$, Hf$_3$C$_2$T$_x$, Zr$_3$C$_2$T$_x$, Cr$_2$CT$_x$, and V$_2$AlC, MXene-based SC electrodes mainly focus on Ti$_3$C$_2$T$_x$, Ti$_2$CT$_x$, Mo$_2$CT$_x$, V$_2$CT$_x$, and MoI$_3$CT$_x$ [20–39]. In addition to having the advantages of numerous electrochemically active sites, intact electron transport channels, and a two-dimensional structure for the diffusion of electrolytes, MXenes also exhibit metal conductivity and contain functional groups, including oxygen and fluorine, which are conducive to current charge–discharge and rate performance [23]. Furthermore, MXenes contribute most capacitance in the form of intercalation pseudocapacitance through intercalation processes with better reversibility and reaction kinetics, showing excellent cycling stability when employed as electrode materials [40]. Since the crystal layers of MXenes are flexible, their large gaps can accommodate more electrolyte ions, and MXenes with high packing density theoretically have higher volumetric capacity and energy density. For example, MXene hydrogels provide a volumetric capacitance of 1500 F cm$^{-3}$, which surpasses the hitherto unequalled value of RuO$_2$, and its rate characteristic is superior to that of carbon [24]. Hence, MXenes, as a layered 2D material, have demonstrated the most promising application potential in flexible SCs because of their higher conductivity and excellent dispersibility, which are beneficial to making films due to their hydrophilic surface. There is also a lot of reported research about MXenes as flexible SC electrode materials.

Several reviews on the synthesis and applications of MXenes have been published, particularly in energy storage and conversion [41–57]. For example, Ma et al. summarized the latest developments in flexible MXene-based composites for wearable devices, emphasizing preparation processes, working mechanisms, performance, and a vast array of applications, including sensors, SCs, and electromagnetic interference (EMI)-shielding materials [58]. Huang et al. reviewed the synthetic processes and fundamental features of functional 2D MXene nanostructures, highlighting their applications in EMI shielding, sensors, photodetectors, and catalysis [59]. Liu et al. overviewed the synthesis methods and the associated mechanisms of the Ti$_3$C$_2$ MXene/graphene composite, highlighting their potential application as energy storage materials, such as lithium–sulfur batteries, lithium-ion batteries, SCs, etc. [53]. Jiang et al. presented the most recent developments in MXene-based microsupercapacitors (MSCs), including device architecture, electrode material design, and different methods of depositing and patterning [41]. In 2021, Xu et al. reviewed recent research and breakthroughs in the chemical and physical synthesis of 2D MXenes and their applications in different flexible devices [50]. Zhang et al. reviewed the most typical flexible electrode materials at this point of development in terms of the recent advancements and challenges of flexible SCs [60]. Ma et al. comprehensively reviewed the most recent developments in Ti$_3$C$_2$T$_x$-based SC electrodes, paying special emphasis to the crucial role played by Ti$_3$C$_2$T$_x$ MXene in the exceptional electrochemical performance as well as the underlying mechanisms [49]. Yang et al. summarized the recent advances in MXene-based electrochemical immunosensors, emphasizing the roles played by MXenes in various types of electrochemical immunosensors [61]. Vasyukova et al. reviewed methods for synthesizing MXenes as well as their potential medical and environmental applications [62]. Yang et al. reviewed the recent research advancements in the structure, construction, and application of MXene-based heterostructures such as SCs, sensors, batteries, and photocatalysts [63]. However, for all that, the above-reported reviews are not specifically for the application of MXene-based electrode materials in flexible SCs.

Despite the numerous reviews that have referred to MXenes for their electrochemical energy storage capabilities, there have been a limited number of reviews about the different construction methods of electrodes for MXene-based flexible SCs. Here, we present the most recent developments in flexible electrode manufacturing and their applications in SCs according to the different construction methods of flexible electrodes based on MXenes and their composite electrodes, with or without substrate support. Firstly, since the distinctive physical and chemical properties of Ti$_3$C$_2$T$_x$ MXene are directly related to the process of preparation, a brief description of the synthesis strategy of Ti$_3$C$_2$T$_x$ MXene and its impact
on the electrochemical properties will be presented. Secondly, construction methods such as self-supporting, PET-supported, fabric fiber-supported, and other substrate-supported MXene-based films as flexible electrodes are reviewed. An overview of the fabrication methods, electrode structures, working mechanisms, electrochemical performance, and related influencing factors of Ti$_3$C$_2$T$_x$-based SC electrodes is provided. In addition, the future possibilities of SC materials based on Ti$_3$C$_2$T$_x$ are outlined to encourage more research and development on MXenes in this fast-growing field.

2. Synthesis of Ti$_3$C$_2$T$_x$ MXene

The outstanding properties of Ti$_3$C$_2$T$_x$ are highly dependent upon its synthesis processes, which determine its chemical composition, electrical conductivity, lateral size, etching efficiency, surface terminations, and defects. Since the first preparation of Ti$_3$C$_2$T$_x$ in 2011, researchers have conducted extensive research on the new MAX phase and on the etching method. At present, many types of etchants are being explored for the production of Ti$_3$C$_2$T$_x$ MXene, including fluoride etching [26,30,64–68], fluoride-based salt etching [69,70], and fluoride-free etching, which have a significant impact on the electrochemical performance.

2.1. HF Etching

MXene is typically prepared by selectively etching the A layer of the MAX phase, and the mechanism can be described as follows [71,72]:

\[ M_{(n+1)}AX_n + 3HF = AlF_3 + 1.5H_2 + M_{(n+1)}X_n \]  
\[ M_{(n+1)}X_n + 2H_2O = M_{(n+1)}X_n(OH)_2 + H_2 \]  
\[ M_{(n+1)}X_n + 2HF = M_{(n+1)}X_nF_2 + H_2 \]

In reaction (1), the A elements are separated from the MAX phase, resulting in the M$_{n+1}$X$_n$ phase. The functional groups of -F and/or -OH originate from reactions (2) and (3). Figure 1a,b show the schematic of the exfoliation process and characterization of structure morphology for Ti$_3$AlC$_2$. Naguib et al. prepared Ti$_3$C$_2$T$_x$ MXene with an accordion-like shape (Figure 1b) by etching Ti$_3$AlC$_2$ powders for 2 h in a 50% concentrated HF solution [73]. Mashtalir et al. investigated the influence of process parameters and particle size on the etching of Al from Ti$_3$AlC$_2$ in a 50% HF solution. The results showed that reducing the initial MAX particle size, prolonging reaction time, and increasing the immersion temperature were advantageous for the phase transformation of bulky Ti$_3$AlC$_2$ into Ti$_3$C$_2$T$_x$ [74]. During the etching procedure, etching duration, temperature, and HF concentration significantly impact the products. Al can be removed from the Ti$_3$AlC$_2$ MAX phase by HF with concentrations as high as 5%. However, an accordion-like particle form is commonly observed when HF concentrations exceed 10%. Moreover, the higher the HF percentage, the more defects there are in the Ti$_3$C$_2$T$_x$ flakes, affecting the quality, stability in the environment, and properties of the MXene obtained [75,76]. As the HF method has a low reaction temperature and is easy to operate, it is ideal for etching Al-containing MAX phases and portions of non-MAX phases. The HF etchant, however, is highly corrosive, toxic, poses operational risks, and has adverse environmental effects.
Figure 1. (a) Schematic of the exfoliation process for Ti$_3$AlC$_2$. (b) SEM image of a sample after HF treatment. Reprinted with permission from Ref. [73]. Copyright 2011 WILEY-VCH Verlag GmbH & Co., KGaA. (c) Ti$_3$AlC$_2$ etched in a solution of HCl + LiF and then washed with water to obtain Ti$_3$C$_2$T$_x$; the resulting Ti$_3$C$_2$T$_x$ behaves like a clay. (d) XRD patterns of samples produced by etching in LiF + HCl solution. Reprinted with permission from Ref. [77]. Copyright 2014 Nature. (e) The schematic illustration of a reaction between Ti$_3$AlC$_2$ and bifluorides. (f) SEM images of samples exfoliated by NH$_4$HF$_2$ and the XRD patterns of Ti$_3$AlC$_2$ and different Ti$_3$C$_2$ samples: (I) Ti$_3$C$_2$ from etching Ti$_3$AlC$_2$ with HF; (II) Ti$_3$C$_2$ from etching Ti$_3$AlC$_2$ with NaHF$_2$; (III) Ti$_3$C$_2$ from etching Ti$_3$AlC$_2$ with KHF$_2$; (IV) Ti$_3$C$_2$ from etching Ti$_3$AlC$_2$ with NH$_4$HF$_2$. Reprinted with permission from Ref. [78]. Copyright 2017 Materials & Design.
2.2. Fluoride-Based Salt Etching

To develop significantly safer and gentler methods to manufacture Ti$_3$C$_2$Tx flakes, researchers attempted to use hydrochloric acid (HCl) and fluoride salts as etchants to dissolve the Al element and generate 2D transition metal carbides. Ghidiu et al. prepared MXenes by dissolving LiF in 6 M HCl (Figure 1c) [77]. Compared to the HF etchant, this method can produce MXene flakes with bigger lateral dimensions, higher yields, and better quality. Furthermore, compared with the lattice parameter of HF-produced Ti$_3$C$_2$Tx (c < 20 Å), the value in this study was 27–28. (Figure 1d). The increased interlayer spacing allows for the creation of more electrochemically active surfaces as well as shorter electrolyte ion transport routes. Furthermore, the milder etchant of LiF + HCl produces the Ti$_3$C$_2$Tx flakes with wider lateral dimensions and fewer nanosized flaws. TEM also showed that the majority of the Ti$_3$C$_2$Tx flakes had diameters of 500–1500 nm. The amount of HCl and LiF during the synthesis of fluoride-based salts affects the size, processing capacity, and quality of Ti$_3$C$_2$Tx. For example, LiF:Ti$_3$AlC$_2$ molar ratios increase from 5 to 7.5 when the HCl concentration is increased from 6 to 9 M, improving the quality and size of the Ti$_3$C$_2$Tx flakes [79].

In addition to LiF, various fluoride salts such as NH$_4$HF$_2$, KF, NaF, FeF$_3$, NH$_4$F, etc., have been utilized to produce Ti$_3$C$_2$Tx MXene. In 2014, it was reported that NH$_4$HF$_2$ could be used to etch sputter-deposited epitaxial Ti$_3$AlC$_2$ films at room temperature [80]. In contrast to the films etched with HF, the films intercalated with NH$_3$ and NH$_4^+$ species showed 25% larger c lattice parameters. Feng et al. described the effect of etching duration and temperature on the synthesis of Ti$_3$C$_2$Tx in 1 M of different bifluoride solutions (NaHF$_2$, KHF$_2$, NH$_4$HF) (Figure 1e) [78]. In 1 M of bifluoride solution at 60 °C, the minimum etching duration for the onset of exfoliation of Ti$_3$AlC$_2$ was 8 h. Using bifluoride, KHF$_2$, or NH$_4$HF$_2$ as an etchant allowed the formation of Ti$_3$C$_2$ with greater interplanar spacing in a single-stage process and the retention of the 2D flake structure (Figure 1f). Wang et al. proposed using iron fluoride (FeF$_3$) and hydrogen chloride (HCl) as an etching for the production of Ti$_{n+1}$C$_n$Tx from Ti$_{n+1}$AlC$_n$ (n = 1 or 2) [81]. Compared to the HF etching method, the fluorine content of Ti$_3$C$_2$ made with FeF$_3$/HCl is lower. By adjusting the immersion time in the water, it was possible to tune the partial oxidation of Ti$_3$C$_2$Tx, which enabled the preparation of a composite of anatase and Ti$_3$C$_2$Tx.

The fluoride salts used in synthesizing Ti$_3$C$_2$Tx are less poisonous and milder than HF. This Ti$_3$C$_2$Tx has a relatively large size, few flaws, a low fluorine concentration, and large interlayer spacing, allowing for further structural modification.

2.3. Fluoride-Free Etching

Even though fluorine-containing etching produces MXenes with a good layer-sheet structure, long etching times can cause defects in the product, and impurity groups (-F, -OH) can change the properties of the MXenes. The specific capacitance of the material can also be affected when it is used as an SC electrode. Researchers have developed a variety of fluorine-free MXene etching techniques in response to these problems [82–89].

Electrochemical etching is a method for preparing 2D Ti$_3$C$_2$Tx with good capacitive performance. This method can be carried out in electrolytes devoid of fluorides in order to produce Ti$_3$C$_2$Tx MXene devoid of fluorine terminations. Al layers can be selectively etched by applying a steady voltage, allowing chloride ions (Cl$^-$) that have a strong affinity for Al to break the Ti-Al bonds. Feng et al. proposed an electrochemical method for layering Ti$_3$C$_2$ using binary aqueous electrolytes [89]. The anodic etching of Al is facilitated by chloride ions, which allow Ti-Al bonds to be broken quickly. Then, ammonium hydroxide (NH$_4$OH) is added to make it easier to etch below the surface of the anode that has already been etched. More than 90% of the Ti$_3$AlC$_2$ etched in a short period of time is a single layer or double layer, and the average lateral dimension exceeds 2 μm. In addition, an all-solid-state SC fabricated from exfoliated sheets exhibits excellent volumetric and areal capacitances of 439 F cm$^{-3}$ and 220 mF cm$^{-2}$, respectively, at a scan rate of 10 mV s$^{-1}$, which is larger than for the classical HF etching process [90].
Alkali is also anticipated to achieve selective etching of the MAX phase. Li et al. successfully prepared multilayer MXene with 92 wt% purity based on the Bayer process using only alkali-assisted hydrothermal methods [91]. Initially, a solution of Ti3AlC2 was oxidized by NaOH and then dissolved into Al (OH)4−, resulting in the surface termination of MXene with various functional groups of Al atoms, such as -OH and/or -O. After that, the inner Al atoms began to oxidize, producing new Al hydroxides ((Al(OH)3) and dehydrated oxide hydroxides (AlO(OH)). These Ti layers provided lattice confinement, preventing these insoluble compounds from reacting readily with -OH to produce dissolvable Al (OH)4−, which interfered with MXene synthesis and had to be eliminated. The schematic diagram of the reaction between Ti3AlC2 and the NaOH aqueous solution under different conditions is shown in Figure 2a. The Ti3C2Tx film electrode was prepared (52 µm thick) in 1 M H2SO4 with a gravimetric capacitance of 314 F g−1 at 2 mV s−1, which is 28.2% higher than the LiF + HCl-Ti3C2Tx clay (75 µm thick) [48] and 214% higher than the HF-Ti3C2Tx [92]. Similarly, Li et al. etched 0.1 g Ti3AlC2 by using 0.35 g of KOH in a hydrothermal reactor at 180 °C for 24 h [93]. Al atoms are replaced with -OH groups, resulting in nanosheets of Ti3C2(OH)2 with significant lateral dimensions. When the MAX phase is etched with concentrated alkali, highly hydrophilic products with F-free terminations can be achieved. The use of high alkali concentrations and high temperatures limits its applications for preparing MXene on a large scale.

Due to their electron acceptor, transition metal halides in the molten state are capable of reacting with the A layer of the MAX phase. As shown in Figure 2b, Li et al. presented a method for etching MAX phases based on direct redox coupling between A and a Lewis acid molten salt cation [94]. This general Lewis acid etching procedure also expanded the range of MAX-phase precursors, which can be used to prepare new MXenes (Figure 2c). These MXenes exhibited increased storage capacity for Li+ and high current in nonaqueous electrolytes, making them suitable electrode materials for Li-ion batteries and multifunctional devices, including capacitors [95,96]. Using the one-step molten salt reaction of SnCl2 in situ, Wu et al. synthesized Ti3C2Tx MXene/Sn composites directly from Ti3AlC2 MAX phase precursors in Figure 2d [97]. The SnCl2 is etched as a Lewis acid during this process to etch the Ti3AlC2 MAX phase and obtain Ti3C2Tx MXenes. The structure of Ti3C2Tx MXene displays a typical accordion design. It was found that the interlayer spacing of Ti3C2Tx MXene was 1.15 nm (Figure 2e), a much greater spacing than that obtained by acid etching (0.96–0.98 nm), widely used at the time. Although the nonaqueous molten salt etching method offers a broader range of etching and chemical safety, it is still in its infancy, which requires further investigation into the physicochemical properties of the MXenes produced.

It is more difficult to produce MXenes using water as a solvent at room temperature. For example, the presence of water adversely affects the synthesis of polymeric nanocomposites with MXenes reinforced by means of in situ polymerization [98,99]. The residual water may have an impact on the successful loading of specific quantum dots onto MXene sheets [100,101]. Moreover, when organic electrolytes are employed, the presence of water could decrease the stability of the electrolyte and reduce the electrochemical voltage window, resulting in the performance degradation of lithium-ion and sodium-ion batteries. In recent years, researchers have made great efforts to find a breakthrough. Using organic substances and deep eutectic solvents (DES) as etching solvents, they have succeeded in preparing MXene products with good electrochemical properties.
As shown in Figure 3a, Wu et al. reported a highly reliable and water-free ion thermal method for synthesizing Ti$_3$C$_2$ MXene in deep eutectic solvents (DES) [102]. The DES used in the production of Ti$_3$C$_2$ MXene offers the following special advantages over earlier high-risk processes: (i) The processing of solid precursors and products at room temperature was highly safe, rather than making use of hazardous solutions; (ii) the low vapor pressure of DES and its excellent solvation properties enable the etching process to generate HF in situ through a reaction between H$_2$C$_2$O$_4$ and NH$_4$F in a mild environment; (iii) the cations of choline were intercalated into the layers of Ti$_3$C$_2$, resulting in a larger interlayer spacing of 1.35 nm in comparison with HF-Ti$_3$C$_2$ (0.98 nm); and (iv) DES can be recycled and reutilized throughout the etching process, which is promising for the industrial preparation of MXene at a low cost. Shi et al. developed a new iodine-assisted nonaqueous etching strategy [103]. MAX powders were immersed in an I$_2$–CH$_3$CN mixture with a 1:3 molar ratio of Ti$_3$AlC$_2$ to I$_2$, as shown in Figure 3b. Iodine can remove Al layers from Ti$_3$AlC$_2$ because Ti–Al bonds are more reactive than Ti–C bonds. Then, manual shaking in an HCl solution was sufficient for the formation of Ti$_3$C$_2$Ti$_6$. The reaction between Ti$_3$C$_2$Ti$_6$ and NaOH water solution under different conditions.

Figure 2. (a) The reaction between Ti$_3$AlC$_2$ and NaOH water solution under different conditions. Reprinted with permission from Ref. [91]. Copyright 2018 WILEY-VCH. (b) Schematic of Ti$_3$C$_2$Tx MXene preparation. (c) Generalization of the Lewis acid etching route to a large family of MAX phases. Reprinted with permission from Ref. [94]. Copyright 2020 Natural Materials. (d) Schematic of the synthesis of Ti$_3$C$_2$Tx and Ti$_3$C$_2$Tx/Sn composites by SnCl$_2$ molten salt reaction. (e) HRTEM image of Ti$_3$C$_2$Tx MXene. Reprinted with permission from Ref. [97]. Copyright 2022 Electrochimica Acta.
for separating 2D MXene sheets. Because of the benefits of the nonaqueous etching process, 2D MXene sheets exhibit good structural stability. MXene films have a higher conductivity of 1250 S cm$^{-1}$ compared to films made with fluoride etchants. The exfoliated MXene sheets, through iodine etching containing extensive oxygen surface groups, can be fabricated into SCs with gravimetric capacitances and cycling stability, which surpasses the performance of most MXene materials previously reported [34,104,105].

**Figure 3.** (a) Scheme of the ionothermal synthesis of DES-Ti$_3$C$_2$ MXene. Reprinted with permission from Ref. [102]. Copyright 2019 Journal of Energy Chemistry. (b) The iodine-assisted etching and delamination of Ti$_3$AlC$_2$ towards 2D MXene sheets. Reprinted with permission from Ref. [103]. Copyright 2021 Wiley-VCH GmbH.

**3. MXene-Based Flexible Electrode Materials**

As electrode materials, MXenes should exhibit not only excellent electrochemical performance but also excellent properties such as hydrophilicity, malleability, and two-dimensional structure (atomic layer thickness and micrometer-scale lateral dimensions), which make them suitable for the formation of the thin film serving as a flexible electrode. As a result, the electrochemical performance of SCs is largely determined by MXene electrode material structure design, such as electrode architecture, surface terminations, interlayer spacing, and composites (Figure 4) [55]. Recently, a lot of research has explored the application of MXenes and their composites for fabricating SCs on different substrates, including self-supporting, PET-supported, carbon-cloth-fiber-supported, and so on. In this section, we provide a report on recent developments in MXene-based flexible electrodes.
3.1. Self-Support MXene-Based Films as Flexible Electrodes

3.1.1. Pure MXene

MXene-based electrodes, especially freestanding MXene films, have immense potential for SCs and flexible electronics [44]. In addition, the many terminations endow MXenes with excellent hydrophilicity and a rich surface charge, allowing MXene nanosheets to be disseminated uniformly in aqueous solutions.

By using vacuum filtration (VAF) [106], the MXene dispersions can be easily turned into MXene films. These films can be directly charged as electrodes for flexible SCs to achieve high specific capacitance and good cycling performance. Ghidiu et al. rolled hydrophilic MXene (Ti$_3$C$_2$) into thin films using LiF and HCl etching [77]. The volumetric capacitance of the Ti$_3$C$_2$ electrode is up to 900 F cm$^{-3}$, which is at least twice that of MXene (300 F cm$^{-3}$) generated through hydrofluoric acid etching and is characterized by exceptional rate performance and excellent cyclability [23]. Furthermore, the synthetic method allows film production to be much faster while avoiding the handling of hazardous concentrated hydrofluoric acid. It is necessary for the delaminated Ti$_3$C$_2$ (d–Ti$_3$C$_2$) films to have a sufficiently high stacking density and electrical conductivity for them to be capable of producing high volumetric performances. As shown in Figure 5a, Que et al. developed a much thinner, more flexible MXene-film electrode obtained through vacuum filtration by applying external pressure to the membrane [107]. The application of external pressures could increase the density of the delaminated Ti$_3$C$_2$ (d–Ti$_3$C$_2$) films, resulting in good wettability, a comparatively high electrical conductivity, and high surface activity, thereby facilitating effective ion transport. The d–Ti$_3$C$_2$ film, pressed at a pressure of 40 MPa, exhibits an extraordinarily high capacitance of 633 F cm$^{-3}$, a high energy density, and outstanding cyclical stability (Figure 5c,d). Furthermore, the corresponding SC in the organic electrolyte has a volumetric energy density of 41 Wh L$^{-1}$ (Figure 5b).
Heat treatment is an efficient approach for eliminating the terminals of MXene and improving its electrochemical performance [108]. A method for enhancing the capacitance performance of Ti$_3$C$_2$Tx film by annealing at a low temperature in inert gas was presented by Zhang et al. [109]. Due to more C−Ti−O active sites and greater interlayer voids, the annealed film at 200 °C in an Ar atmosphere has an energy density of 29.2 Wh Kg$^{-1}$ and a capacitance of 429 F g$^{-1}$ in 1 M H$_2$SO$_4$ electrolyte. Subsequently, Zhao et al. investigated the high-temperature annealing of Ti$_3$C$_2$Tx films to enhance capacitance performance [110]. In addition to its gravimetric value of 442 F g$^{-1}$, the film also has a high volumetric capacitance and an excellent rate capability after being annealed at 650 °C in an Ar atmosphere. As a simple and environmentally friendly process, alkalinizing followed by annealing has been certified to increase the gravimetric capacitance of MXenes. By alkalinizing and annealing Ti$_3$C$_2$Tx film (Figure 6a), Zhang et al. synthesized a flexible and binderless MXene film (named ak−Ti$_3$C$_2$Tx film−A) [106]. As a result of the alkalinizing and annealing processes, more oxygen-containing groups are exposed to the aqueous electrolyte, increasing the pseudocapacitance during the charge−discharge process [111,112]. Furthermore, the annealing treatment also increases the crystalline order, which enhances the conductivity of the MXene film. In addition to extremely high volumetric capacitance (Figure 6b), the film electrode has remarkable cycling stability. The symmetric SC with ak−Ti$_3$C$_2$Tx film−A also showed a volumetric energy density of 45.2 Wh L$^{-1}$. 

Figure 5. (a) Schematic illustration of the high-pressure d−Ti$_3$C$_2$ film synthesis and electrode preparation. (b) Ragone plots of volumetric energy and power densities. (c) Volumetric capacitances of the d−Ti$_3$C$_2$ film electrodes in different symmetric SCs. (d) Ragone plots of volumetric energy and power densities obtained from the symmetric SCs based on the d−Ti$_3$C$_2$ films under different pressures. Reprinted with permission from Ref. [107]. Copyright 2018 WILEY-VCH Verlag GmbH & Co., KGaA.
Although MXenes can be easily built into a film using a simple vacuum filtration process, this results in the horizontal restacking of the delaminated MXene nanosheets, slowing ion transport as well as inadequate active site exposure, hence reducing capacitance and rate performance. Many ways have been reported for enhancing ion accessibility to active sites. For example, the freeze-drying treatment is an efficient way of producing 2D materials with extremely complex structures since some of the metastable designs can be preserved during the process [114]. During the process, the solvent molecules function as pore creators, which prevent the flakes from stacking, resulting in an increase in the specific surface area. Additionally, MXene films with suitable porosity architectures can be produced by modifying the freeze-drying procedure. Xia et al. presented a method for fabricating a Ti₃C₂Tx film electrode with malleable, freestanding, and vertically aligned properties by mechanically shearing a liquid–crystalline phase of MXene nanosheets and then freeze-drying the nanosheets to remove ethanol [115]. Ran et al. fabricated freestanding and flexible MXene films with vacuum-filtering and freeze-drying techniques (Figure 6c) [113]. The frozen solvent molecules were eliminated by sublimation throughout the freeze-drying process, mitigating the detrimental effect of van der Waals forces and enhancing layer spacing for fabricating freestanding and vertically aligned properties by mechanically shearing a liquid–crystalline phase of MXene nanosheets and then freeze-drying the nanosheets to remove ethanol [115]. Ran et al. fabricated freestanding and mechanically shearing a liquid–crystalline phase of MXene nanosheets and then freeze-drying procedure. Xia et al. presented a method for fabricating a Ti₃C₂Tx film electrode with malleable, freestanding, and vertically aligned properties by mechanically shearing a liquid–crystalline phase of MXene nanosheets and then freeze-drying the nanosheets to remove ethanol [115]. Ran et al. fabricated freestanding and flexible MXene films with vacuum-filtering and freeze-drying techniques (Figure 6c) [113]. The frozen solvent molecules were eliminated by sublimation throughout the freeze-drying

Figure 6. (a) Schematic diagram showing the synthesis process of ak–Ti₃C₂Tx film–A. (b) The specific capacitance as a function of current density. Reprinted with permission from Ref. [106]. Copyright 2018 Electrochimica Acta. (e) Schematic illustration for the fabrication of f-MXene and v-MXene films. (d) Specific capacitance of f–MXene–10 and v–MXene–10 at different current densities. Reprinted with permission from Ref. [113]. Copyright 2020 Applied Surface Science. (e) SEM image of macroporous templated Ti₃C₂Tx electrode cross-section. Insets show schematically the ionic current pathway in electrodes of different architectures. (f) Cyclic voltammetry profiles of a macroporous 13–µm–thick film with a 0.43 mg cm⁻² loading collected in 3 M H₂SO₄ at scan rates from 20 to 10,000 mV s⁻¹; the inset shows a schematically macroporous electrode architecture and the ionic current pathways in it. Reprinted with permission from Ref. [24]. Copyright 2017 Nature Energy.
process, mitigating the detrimental effect of van der Waals forces and enhancing layer spacing. In comparison to the dense stacking of vacuum-heated MXene (v-MXene) film, the freeze-dried MXene (f-MXene) film exhibited a porous structure that enhanced electrolyte ion shuttling, thus enhancing electrochemical performance. Therefore, the f-MXene film electrode has a maximum specific capacitance of 341.5 F g\(^{-1}\) at 1 A g\(^{-1}\) and 206.2 F g\(^{-1}\) when the current density reaches 10 A g\(^{-1}\), which is a significant improvement over the v-MXene film electrode (Figure 6d).

The templating method is also widely used to produce porous 2D materials by putting a template material into the nanosheet interlayers of 2D materials and then removing it [115–117]. Typically, polymers are utilized as templates for designing 3D macroporous electrode films by ordered assembly. Lukatskaya et al. created a flexible Ti\(_3\)C\(_2\)T\(_x\) electrode with an open, porous architecture using microspheres of polymethylmethacrylate (PMMA) as a sacrificial template and then removed the template via annealing (Figure 6e) [24]. The Ti\(_3\)C\(_2\)T\(_x\) electrode exhibited a capacitance of 200 F g\(^{-1}\) at scan rates as high as 10 V s\(^{-1}\) (Figure 6f).

3.1.2. MXene/Graphene

Integrating MXenes with graphene is a promising method of fabricating composite films. The irregular Ti\(_3\)C\(_2\)T\(_x\) acts as an intercalator and dispersant within the graphene layer, lessening graphene agglomeration and increasing specific surface area. The Ti\(_3\)C\(_2\)T\(_x\) with superior electrical conductivity and hydrophilicity will enhance the electrochemical properties of the composites and their capacitive deionization characteristics [118–120]. Thus, the synergistic effect enabled by the bilayer effect of graphene and the pseudocapacitive characteristics of Ti\(_3\)C\(_2\)T\(_x\) may enhance the energy storage performance of the composite electrode [121–125].

Most of the time, MXenes and graphene are made by mixing solutions of MXenes with reduced graphene oxide (rGO) or graphene oxide nanosheets and then vacuum-filtering to form the composite films [126–129]. Yan et al. came up with a way to make MXene/rGO SC electrodes using the electrostatic self-assembly of negatively charged MXene and positively charged, chemically oxidized rGO, as shown in Figure 7a [130]. The MXene/rGO composite effectively prevents the self-restacking of both rGO and MXene while maintaining extremely high electrical conductivity (2261 S cm\(^{-1}\)) and large density (3.1 g cm\(^{-3}\)). The MXene/rGO-5 wt% composite electrode has an excellent volumetric capacitance at 2 mV s\(^{-1}\), a capacitance retention capacity of 61% at 1 V s\(^{-1}\), and an extended cycle life. In addition, this binder-free symmetric SC displays an extremely high volumetric energy density of 32.6 Wh L\(^{-1}\). Fan et al. prepared modified MXene/holed graphene films by filtering alkalized MXene and holey graphene oxide (HGO) dispersions and annealing them in Figure 7b [128]. Alkali is capable of leading not only to the destruction of charge balance in holey graphene oxide and MXene dispersions but also of causing the transition of the -F group into a -OH group. Furthermore, annealing may also remove most of the -OH groups and increase the number of Ti atoms, which could lead to greater pseudocapacitive reactions. It can provide extremely high capacitances (1445 F cm\(^{-3}\) at 2 mV s\(^{-1}\)), high mass loading capacities, and excellent rate performance as an electrode material for SCs. Furthermore, the assembled symmetric SC exhibits a tremendous volumetric energy density (38.5 Wh L\(^{-1}\)).
These heterostructured films were manufactured via a vacuum-assisted filtration process, which is both time-consuming and size-constrained, making it unsuitable for large-scale production. Therefore, for a satisfactory stacking of each component, as well as for high-speed processing [131], Miao et al. developed a simple and effective method for fabricating a 3D porous MXene film using self-propagating reduction. The process can be completed in 1.25 s, resulting in a 3D porous framework via the immediate release of substantial amounts of gas. MXene/rGO films have a higher capacitance and rate performance because the 3D porous structure provides abundant ion-accessible active sites and allows rapid ion transport [132]. Yang et al. developed an effective and rapid self-assembly method for creating a 3D porous oxidation-resistant MXene/graphene (PMG) composite using the template in Figure 8a [133]. The 3D porous design could successfully prevent the oxidation of MXene layers, ensuring superior electrical conductivity and an adequate number of electrochemically active sites. Therefore, the PMG−5 electrode has an exceptional cycling stability, excellent rate performance, and a remarkable specific capacitance (Figure 8b,c). In addition, the as-assembled asymmetric SC (ASC) has excellent cycling stability with a specific capacitance degradation of 4.3% after 10,000 cycles and a notable energy density of 50.8 Wh kg⁻¹ (Figure 8d,e).
3.1.3. MXene/Carbon Nanotubes

Carbon nanotubes (CNTs), a common and well-studied type of 1D carbon nanomaterial, are also used to make SC electrodes by combining them with Ti$_3$C$_2$Tx MXene. CNTs can increase the performance of energy storage by enlarging the specific surface area, regulating the interlayer gap, enabling ion diffusion, and improving electrical conductivity [134–139].

The layer-by-layer assembly method is a well-established method of constructing microstructures [140,141]. Zhao et al. have exploited sandwich-like, flexible MXene/CNT film electrodes for SCs using the alternate filtration of MXene and CNTs from aqueous solutions (Figure 9a) [142]. In comparison to pure MXene and randomly mixed MXene/CNT paper electrodes, these electrodes are highly flexible and freestanding, with highly significant volumetric capacitances and excellent rate performance. At a scan rate of 2 mV s$^{-1}$, the MXene/SWCNT paper electrode showed a high capacitance of 390 F cm$^{-3}$. It also displayed a volumetric capacitance of 350 F cm$^{-3}$ at 5 A g$^{-1}$, which did not degrade after 10,000 cycles (Figure 9b,c).

Self-assembly technology, also known as electrostatic assembly, is an easy method of synthesizing hybrid materials. In self-assembly technology, one material is constructed on the surface of another, thus forming composites by utilizing the electrostatic interaction between distinct charges. Dall’Agnese et al. produced a flexible Ti$_3$C$_2$Tx/CNT film by using the self-assembly approach and studied the electrochemical behavior of Ti$_3$C$_2$ MXene in different organic electrolytes [143]. This electrode exhibited excellent cycling
stability and rate performance. By means of vacuum filtration, Xu et al. also produced a Ti$_3$C$_2$Tx/SCNT self-assembled composite electrode, which exhibited a capacitance of 220 mF cm$^{-2}$ (314 F cm$^{-2}$) and retained 95% of its capacitance after 10,000 cycles [144]. The enhanced capacitance could be attributed to the increase in the interlayer spacing of MXene and the improved ion accessibility brought about by the utilization of SWCNTs as spacers.

Even though the MXene/MWCNT composite electrodes made with these methods seem to have a larger gap between layers compared to unmodified MXenes, the 2D layers continue to be horizontally stacked, indicating that the stacking problem persists, which restricts ion accessibility and slows ion kinetics. As shown in Figure 9d, Zhang fabricated a flexible 3D porous Ti$_3$C$_2$Tx/CNTs film (3D–PMCF) using an in situ ice template strat-

![Figure 9.](image-url)
After freeze-drying, the resulting Ti$_3$C$_2$Tx/CNTs film possessed a 3D structural network with a highly porous structure, which was templated by interlayered ice in conjunction with CNTs as functional spacers. In addition to exposing several active sites, 3D-PMCF facilitates rapid ion transport, resulting in superior electrochemical performance. The symmetric SCs based on 3D–PMCF achieved a high energy density of 23.9 Wh kg$^{-1}$, demonstrating their potential as flexible electrodes for supercapacitors (Figure 9e). In order to achieve improved ion transport at low temperatures, Gao applied knotted CNTs, which broke the traditional horizontal alignment of the 2D layers of MXene Ti$_3$C$_2$ [145]. As a result of knot-like structures, the Ti$_3$C$_2$ flakes are prevented from restacking, providing fast pathways for ion transport, which results in the improved low-temperature operation of Ti$_3$C$_2$ MXene-based SCs (Figure 9f,g).

3.1.4. MXene/Polymer

Since polymers are simple to produce, are inexpensive, and have tunable functionalities, they have been widely employed to prepare MXene-based composites [146,147]. MXene and polymer-formed composite films have also been increasingly applied to flexible devices over the past few years.

Solvent processing is the most common method of production. In most cases, MXene is added to a polymer solution in the colloidal form (often aqueous). Then, the solvent is removed from the solution using evaporation, vacuum filtration, or precipitation into a nonsolvent. Ling et al. fabricated Ti$_3$C$_2$/polymer membranes by applying charged polydiallyldimethylammonium chloride (PDDA) and polyvinyl alcohol (PVA) via a VAF method (Figure 10a) [148]. Compared to pure Ti$_3$C$_2$Tx film ($2.4 \times 10^5$ S m$^{-1}$), the conductivity of Ti$_3$C$_2$Tx/PVA composite film is $2.2 \times 10^4$ S m$^{-1}$. However, the composite Ti$_3$C$_2$Tx/PVA films displayed a significantly higher tensile strength than the pure PVA or Ti$_3$C$_2$Tx films (Figure 10b). Intercalating and confining the polymer between the MXene flakes helped increase both cationic intercalation and flexibility, resulting in an outstanding volumetric capacitance (Figure 10c). The volumetric capacitance was still quite respectable after 10,000 cycles, indicating satisfactory cyclic stability (Figure 10d). In addition, as shown in Figure 10d, Boota et al. fabricated a Ti$_3$C$_2$/polypyrrole (PPy) flexible film by using the oxidant-free polymerization of PPy and a subsequent VAF approach [149]. By intercalating homogeneous polymer chains, the interlayer spacing is widened, and the orderly alignment of the polymer chains facilitates charge transport and ion diffusion within the electrolyte, significantly enhancing the pseudocapacitive. As SC electrodes, the PPy/Ti$_3$C$_2$Tx film retained a capacitance of 92% after 25,000 cycles and showed an excellent volumetric capacitance of 1000 F cm$^{-3}$ (Figure 10e). In Figure 10f, Luo et al. presented the simple physical mixing of MXene nanosheets with PANI nanofibers followed by a suction filtration procedure to create MXene/PANI films [150]. In addition to offering a channel for charge carriers, PANI nanofibers can enhance MXene layer spacing, which is advantageous for electrolyte ion infiltration. The assembled device exhibited a specific capacitance of 272.5 F g$^{-1}$ at 1 A g$^{-1}$ (Figure 10g).

It is more convenient and less expensive in industrial production to directly combine a Ti$_3$C$_2$Tx supernatant with PEDOT aqueous solution than to polymerize a monomer in situ on the sheet surface. Li et al. proposed an SC constructed from a Ti$_3$C$_2$/poly (3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS) membrane treated with sulfuric acid (H$_2$SO$_4$), with the hybrid film serving as the negative electrode [151]. H$_2$SO$_4$ can remove a portion of the insulating PSS, which results in an increased conductivity in the composite. As well as providing electroactive surfaces, PEDOT chains create electronic transport pathways that accelerate electrochemical reactions. In comparison to pure Ti$_3$C$_2$, the hybrid film has an increase in specific surface area of 4.5 times, as well as exceptional volumetric capacitance (1065 F cm$^{-3}$ at 2 mV s$^{-1}$).
3.1.5. MXene/Metal Oxides, Metal Hydroxide Composites

Transition metal compounds have large specific capacitances in theory (RuO$_2$ (720 F g$^{-1}$), MnO$_2$ (1370 F g$^{-1}$), and MoS$_2$ (811 F g$^{-1}$)). However, the rate performance and cycle stability are not good when using these compounds alone [152–155]. The conductivity of MXenes is high, while the capacitance is relatively low in comparison with transition metal compounds. The integration of pseudocapacitive materials and MXenes will enhance the pseudocapacitance. As a pseudocapacitive material, oxide/hydroxide nanoparticles are used as intercalation materials to prevent the restacking of MXene sheets [156–161].

As a typical pseudocapacitive material, MnO$_2$ possesses plentiful resources, low toxicity, low cost, and high capacitance in theory. In addition to enhancing its conducting properties, the MnO$_2$/MXene composite can achieve higher specific capacitances. Tian et al. exploited freestanding and flexible MnO$_2$–Ti$_3$C$_2$ films using a simple in situ wet-chemistry synthesis approach [162]. In comparison to random mixing approaches or layer-by-layer synthesis approaches [162].
assembly, this method ensures a strong connection between the components, thus reducing contact resistance and improving electrochemical performance. The MnO$_x$-Ti$_3$C$_2$ film electrodes exhibited outstanding electrochemical properties. In addition to a volumetric capacity of 602.0 mF cm$^{-2}$, they also show good rate capability. The MnO$_x$-Ti$_3$C$_2$ film-based symmetric SC has an energy density of 13.64 mWh cm$^{-3}$ at 2 mV s$^{-1}$, a power density of 3755.61 mW cm$^{-3}$ at 100 mV s$^{-1}$, and remarkable cycling stability. As shown in Figure 11a, Zhou et al. made a highly flexible, all-pseudocapacitive electrode by combining Ti$_3$C$_2$Tx with ultralong MnO$_2$ NWs [158]. MnO$_2$ nanosheets can be useful as electrochemically active materials and interlayers for preventing MXene restacking and improving pseudocapacitance, as well as retaining outstanding flexibility. When used as an electrode for SCs, the resulting film (Ti$_3$C$_2$Tx/MnO$_2$ = 6) has excellent volumetric and a specific areal capacitance of 1025 F cm$^{-2}$ and 205 mF cm$^{-2}$, respectively (Figure 11b). It also retains its capacitance after 10,000 cycles at 98.38% and has high capacitance retention, outperforming the previously reported Ti$_3$C$_2$Tx MXene-based flexible electrodes.

![Figure 11](https://example.com/figure11.png)

**Figure 11.** (a) A schematic representation of the fabrication process. (b) Specific areal capacitance of different samples versus current density. Reprinted with permission from Ref. [158]. Copyright 2018 WILEY-VCH Verlag GmbH & Co., KGaA. (c) Schematic illustration of the synthesis of Ti$_3$C$_2$/FeOOH hybrid films. (d) The areal capacitance as a function of scan rates. (e) Ragone plots of the Ti$_3$C$_2$/Fe-$15\%$//MnO$_2$/CC device in comparison with the other reported ASCs. Reprinted with permission from Ref. [163]. Copyright 2019 Electrochimica Acta. (f) Schematic illustration of the fabrication process of M/MoO$_3$ hybrid films. (g) Corresponding volumetric specific capacitance of various electrodes. Reprinted with permission from Ref. [164]. Copyright 2020 Nano-Micro Lett.
Zhao et al. synthesized a freestanding Ti₃C₂/FeOOH quantum dots (QDs) hybrid film by electrostatic self-assembly in Figure 11c [163]. Amorphous FeOOH QDs anchored on Ti₃C₂ nanosheets can serve as both pillars to prevent the nanosheets from being restacked as well as active materials to provide considerable capacitance. Ti₃C₂ nanosheets as conductive layers were used to make up for the low conductivity of FeOOH. In addition to possessing a capacitance that is 2.3 times higher than the traditional Ti₃C₂ film, the hybrid Ti₃C₂/FeOOH QDs film shows excellent cycle stability with neutral electrolytes (Figure 11d). An ASC was created by combing the hybrid film with MnO₂/CC. The ASC provided a maximum power density of 8.2 mW cm⁻² and an energy density of 42 µWh cm⁻² when working in a wide potential window of 1.6 V (Figure 11e). Simple, flexible devices made from Ti₃C₂/Fe−15%/MnO₂/CC demonstrated outstanding flexibility. These results show that the Ti₃C₂/Fe−15% hybrid film has a lot of potential for use in flexible ASCs, where it will allow for a larger applied potential difference window and a higher energy density.

MoO₃ nanobelts, as pseudocapacitive materials, exhibit excellent potential for MXene films, such as mechanical stability, simple preparation procedure, strong electrochemical reaction activity, and high pseudocapacitance in acidic conditions. As depicted in Figure 11f, Wang et al. manufactured all-pseudocapacitive and highly malleable MXene/MoO₃ hybrid films using a vacuum-assisted technique. [164]. As a result of the excellent synergetic effect, the MXene nanosheets exhibit the highest pseudocapacitance in an acidic electrolyte. The as-prepared freestanding MXene/MoO₃-20% hybrid film exhibits an extremely high volumetric capacitance of 1817 F cm⁻³, which is over 1.5 times greater than the capacitance of pure MXene film (Figure 11g).

3.2. PET (Terephthalic Acid Glycol Ester) as Flexible Substrate

Due to their good flexibility and stability, polymers are commonly used as substrate materials for flexible SCs [165, 166]. Flexible SCs are typically constructed by combining conductive materials with PET flexible substrates through deposition, spraying, printing, and coating processes.

As shown in Figure 12a, Rosen et al. fabricated a high-performance solid-state SC from Mo₁.₃₃C MXene/PEDOT:PSS-aligned polymer films [167]. This process involved vacuum-filtering the composite, followed by acid treating the as-obtained film for 24 h before preparing the all-solid SCs using PET as a flexible substrate. PEDOT nanofibers are aligned and confined between layers of high-conducting Mo₁.₃₃C, allowing rapidly reversible oxidation reactions as well as short diffusion paths to facilitate ion transport. Thus, these flexible solid-state SCs have a maximal capacitance of 568 F cm⁻³, a power density of 19,470 mW cm⁻³ (Figure 12b), an extremely high energy density of 33.2 mWh cm⁻³, and a capacitive retention of 90% after 10,000 cycles. As shown in Figure 12c, a flexible hybrid film electrode composed of 3D cubic Ni-Fe oxide and 2D Ti₃C₂Tx layers was developed by Zhang et al. [157], and it was made to adhere to a PET flexible substrate for the purposes of electrochemical measurements. MXene layers were utilized as binders and conductive additives to assist charge transfer in the electrode, thereby preventing a substantial loss in conductivity. As a result of the cubic Ni-Fe oxide being used as a spacer between the MXene layers, more interlayer space was created, which improved the diffusion of electrolytes. Based on the flexible composite film electrode, a solid-state flexible SC was fabricated that displays exceptionally robust cycling stability, retaining 90% of its capacitance after 10,000 charging–discharging cycles and maintaining steady energy storage capability following 50 cycles of mechanical bending.
Zhang et al. produced transparent films by spin-casting colloidal solutions of Ti$_3$C$_2$T$_x$ nanosheets onto PET substrates and then annealing them at 200 °C [168] (Figure 12d). The DC conductivity of films with transmissions of 29% and 93%, respectively, is 9880 S cm$^{-1}$ and 5736 S cm$^{-1}$. These transparent Ti$_3$C$_2$T$_x$ electrodes have an excellent volumetric capacitance in combination with a high response speed. Transparent solid-state asymmetric SCs have a greater energy density (0.05 μWh cm$^{-2}$) and capacitance (1.6 mF cm$^{-2}$) than SWCNT or graphene-based transparent SC devices, as well as a longer lifetime. Jiang et al. constructed an asymmetric flexible SC by coating the slurry of MnO$_2$/Ti$_3$C$_2$T$_x$ on PET substrates [169] (Figure 12e). This highly synergistic effect between Ti$_3$C$_2$T$_x$ and MnO$_2$, resulting from their chemical interaction, significantly enhances structural stability, rate stability, and the specific capacitance of the MnO$_2$/Ti$_3$C$_2$T$_x$ nanocomposite electrode. Furthermore, a symmetrical flexible SC based on a MnO$_2$/Ti$_3$C$_2$T$_x$ nanocomposite electrode exhibits good electrochemical performance, great flexibility, and excellent cycling ability.

In addition to being flexible, SCs are also expected to be miniature in order to power microdevices. The construction of flexible MSCs is also a future development trend. Laser
scribing is a straightforward and cost-effective method for creating unique patterns on a variety of substrates. It has excellent flexibility in the depth of the field and the materials that can be ablated. The difficulty of laser processing is finding the correct wavelength, pulse energy, and scanning speed of the laser to achieve the proper resolution. Huang et al. described a laser processing method for fabricating freestanding MXene films, then mounted MXene films on PET substrates for flexible MSC device manufacturing, as in Figure 13a [170]. Since a cool laser is employed, less oxidation and no undesirable edge defects have been discovered during the process of laser scribing, which has improved the performance of the as-made MSC device. Moreover, the areal capacitance of these freestanding flexible MSCs is an astounding 340 mF cm\(^{-2}\) at 0.25 mA cm\(^{-2}\) when polyvinyl alcohol/sulfuric acid (PVA/H\(_2\)SO\(_4\)) gel is used as the electrolyte. As the device bends to 60\(^\circ\), it does not show any decrease in capacitance. In addition, MSCs also show the highest energy density and volumetric capacitance among (at the time) all unconventional SCs, reaching 12.4 mWh cm\(^{-3}\) and 183 F cm\(^{-3}\), respectively.

![Schematic illustration of manufacturing flexible solid-state MSCs.](image)

**Figure 13.** (a) Schematic illustration of manufacturing flexible solid-state MSCs. Reprinted with permission from Ref. [170]. Copyright 2018 WILEY-VCH Verlag GmbH & Co., KGaA. (b) Schematic illustration of direct MXene ink printing. Reprinted with permission from Ref. [170]. Copyright 2019 Nature Communications. (c) Schematic diagram of the inkjet printing of MXene/graphene films. Reprinted with permission from Ref. [171]. Copyright 2022 Journal of Alloys and Compounds. (d) Asymmetrical MXene MSCs fabricated by a modified screen-printing process. Reprinted with permission from Ref. [172]. Copyright 2022 Copyright 2018 Nano Energy. (e) The fabrication process of 3D printing all-MXene MSC via MSES. (f) Photographs of a 3D-printed MXene MSC; scale bar is 1 cm. Reprinted with permission from Ref. [173]. Copyright 2021 Wiley-VCH GmbH.
Inkjet printing is one of the most promising technologies for the speedy development and application of new material inks. In addition to the excellent printing precision that can be provided on a variety of substrates, its printing speed is also faster than that of screenprinting. Zhang et al. reported employing inkjet printing on an AlO$_x$-coated PET substrate to produce an MSC (Figure 13b) [166]. A variety of solvents have been investigated for fine printing, such as NMP, ethanol, DMSO, and DMF. Both low- and high-concentration inks show excellent printing resolution. The MSC has a volumetric capacitance of 562 F cm$^{-3}$, while its energy density is 0.32 µWh cm$^{-2}$, considered to be one of the highest among printed MSC devices. Wen et al. fabricated flexible MXene/graphene composite electrodes through inkjet printing (Figure 13c) [171]. As a result of the insertion of graphene nanosheets into composite films, the interlayer gap can be increased, thereby minimizing the self-stacking effect of MXenes. The composite electrodes exhibited high volumetric capacitance and excellent stability. Moreover, a flexible MSC based on the composite electrodes demonstrated a competitive energy density.

Due to its reproducibility and stability, screen-printing is employed for the mass production of MSCs. In this technique, a stencil is initially placed over the desired substrate, followed by the ink being pressed through a planar form stencil onto the substrate. Subsequently, the ink dries to form the desired patterns on the substrate. As shown in Figure 13d, Xu et al. fabricated a flexible coplanar asymmetric microscale hybrid device by screen-printing on PET substrates [172]. The assembled flexible device has excellent areal energy and power densities.

The 3D printing method is regarded to be a form of additive manufacturing. Extrusion-based 3D printing is the most cost-effective and versatile method for producing 3D and self-supported micro-prototypes compared with other 3D printing methods [174,175]. An extrusion-based 3D printing requires a functional ink material that is high in viscosity and exhibits the proper rheological behavior in order to achieve rapid and precise prototyping [176]. Huang et al. performed an extrusion-based 3D printing of MXene ink using a 3D printing station and then produced an MSC with interdigital patterns using a layer-by-layer printing procedure on PET substrates (Figure 13e,f) [173]. The MSC exhibits a record-high energy density of 0.1 mWh cm$^{-2}$ at 0.38 mW cm$^{-2}$ and excellent areal capacitance (2.0 F cm$^{-2}$ at 1.2 mA cm$^{-2}$).

In addition to the fabrication techniques discussed above, Feng et al. created in-plane flexible MSCs by spray coating MXene/rGO hybrid ink onto a PET substrate [121]. The flexible MSCs have a volumetric capacitance of 33 F cm$^{-3}$ and an area capacitance of 3.26 mF cm$^{-2}$ at 2 mV s$^{-1}$.Couly et al. fabricated an asymmetric MXene-based MSC that is current-collector-free, binder-free, and flexible by spraying both Ti$_3$C$_2$T$_x$ and rGO dispersions onto a PET substrate [177]. Despite operating for 10,000 cycles, this MXene-based asymmetric MSC retains 97% of its initial capacitance. It also has a power density of 0.2 W cm$^{-3}$ and an energy density of 8.6 mWh cm$^{-3}$.

An electrolyte is also an essential part of constructing flexible SCs. SCs that are flexible work in a bent state, which can potentially result in electrolyte leakage. This necessitates the development of an electrolyte with high conductivity and excellent infiltration characteristics. Moreover, in order to further expand the electrochemical voltage window of the flexible MSCs based on MXenes, Zheng et al. created ionogel-based MXene MSCs with a MXene film that was pre-intercalated by the ionic liquid. The patterned MXene-based microelectrodes were transferred onto a PET substrate to fabricate MSCs with the assistance of 20 MPa pressure [178]. Due to the pre-intercalation of an ionic liquid, the interlayer spacing was enlarged to 1.45 nm, which was beneficial to the ion deintercalation and intercalation of the electrolyte. The MXene-based MSCs (M−MSCs) using EMIMBF$_4$ ionic liquid as an electrolyte showed high areal energy density and remarkably high volumetric capacitance. In addition, the solid-state M−MSCs with ionogel as an electrolyte exhibited a volumetric energy density of 41.8 mWh cm$^{-3}$ and an excellent areal energy density of 13.3 Wh cm$^{-2}$, as well as long-term cyclability.
3.3. Fabric Fiber as Flexible Substrate

Because fabric fibers have stable chemical properties, high electrical conductivity, and good mechanical properties, they can be used as current collectors for flexible substrates to support or load active materials for the construction of flexible energy storage devices. Fibers have the advantage of containing 3D open-pore structures, which makes conformal coating much more effective throughout the textile network, leading to a much higher loading of active materials and, accordingly, higher energy density and power. In addition, fabric fibers are thermally stable, which expands the temperature range of flexible SCs. As a consequence, there are numerous approaches to constructing flexible electrodes based on fiber textiles, such as through chemical vapor deposition (CVD), electrodeposition, dipping, and spin coating active electrode material onto fiber textiles.

Specifically, Xia et al. presented a simple CVD method that can produce single-crystalline TiC nanowire arrays with good electrical conductivity directly on flexible carbon cloth [179]. The TiC nanowire arrays demonstrated excellent performance for flexible SCs over a wide temperature range (–25 °C to 60 °C), including high-rate characteristics and an ultra-stable cycle life. In addition, the energy density of TiC-based SCs was 18.2, which is roughly double that of commercial AC-based SCs.

Electrophoretic deposition (EPD) can be used to fabricate binder-free films with uniformity and mass-loading adjustability. Furthermore, the preparation method of EPD has unique advantages in infiltrating and depositing active material onto porous substrates, especially for the production of wearable SCs on flexible substrates. Xu et al. deposited binder-free d-Ti₃C₂Tx nanoflakes on a fabric substrate in acetone solvent utilizing the EPD approach [180]. As the surface of MXene flakes that contain absorbed H⁺ carries positive charges, the flakes migrate toward the cathode during the deposition of electrophoretic particles, resulting in a uniform film of MXene. In addition to great flexibility, all-solid-state SCs based on EPD film electrodes display exceptional electrochemical performance. Wang et al. employed the electrophoresis effect in depositing Ti₃C₂Tx/rGO composite on carbon cloth. Without adhesives, the built solid-state SCs based on the Ti₃C₂Tx/rGO electrode displayed outstanding cycling stability, low series resistance, high specific capacitance, and excellent mechanical flexibility [181].

In addition to deposition, dipping is a more convenient and efficient method of constructing flexible electrodes on fabric substrates [182,183]. Yan et al. fabricated conductive textile electrodes that have a specific capacitance of 182.70 F g⁻¹ using dipping and drying [184]. PPy textile electrodes were electrochemically deposited on MXene textiles as a means of improving the capacitance of MXene and avoiding MXene oxidation. Furthermore, the symmetrical solid-state SCs using MXene-PPy textile electrodes also showed improved electrochemical performance and a greater degree of flexibility. Li et al. developed a synthetic technique for the construction of a high-performance, flexible SC by the in situ growth of multi-walled carbon nanotubes (MWCNTs) on MXene nanosheets placed on a CC substrate [185] (Figure 14a). Similarly, a specific concentration of MXene was loaded onto CC with multiple dipping and drying, catalyzed by nickel-aluminum-layered double hydroxide (Ni-Al-LDH), and then subjected to CVD to produce MWCNTs. The MWCNT-MXene@CC displays excellent conductivity along with an exfoliated, large surface area. Therefore, the as-manufactured electrode exhibited a large specific capacitance while retaining a high retention after 16,000 cycles at 10 mA cm⁻² (Figure 14b,c). Recently, Li et al. developed an extremely conductive textile based on MXenes through electrostatic self-assembly [186]. In addition to providing abundant active sites, the horizontally aligned, compact MXene flakes painted on the fabric fibers may produce connected electron transport channels, as shown in Figure 14d. Thus, from 1 to 50 mA cm⁻², the MXene/PEI-modified fiber fabric (MXene/PMFF) delivered excellent rate performance with no reduction in capacitance. The PPy-coated MXene/PMFF electrode had a high-rate capability and areal capacitance as well as outstanding cycling stability and gravimetric capacitance (Figure 14e,f). Moreover, a solid-state symmetric SC based on the
PPy/MXene/PMFF textiles had an energy density of 40.7 Wh cm\(^{-2}\), a maximum power density of 25 mW cm\(^{-2}\), as well as an areal capacitance of 458 mF cm\(^{-2}\).

Figure 14. (a) Schematic illustration for the preparation of MXene and MWCNTs. (b) Areal specific capacitance of different samples at different scan rates. (c) Cycling stability of 10–MWCNT–MXene@CC electrode at a current density of 10 mA cm\(^{-2}\). Reprinted with permission from Ref. [185]. Copyright 2020 WILEY-VCH Verlag GmbH & Co., KGaA. (d) Schematic illustration of the synthesis process for a MXene and PPy/MXene/PMFF textile electrode. (e) Areal capacitance comparison of the samples at different current densities. (f) Cycling performance of PPy/FF and PPy/MXene/PMFF measured at 30 mA cm\(^{-2}\), with enlargement of cycling performance of PPy/FF in the inset. Reprinted with permission from Ref. [186]. Copyright 2020 Energy Storage Materials.

3.4. Other Substrates

In addition to the usual PET and fabric flexible substrates, others, such as PDMS substrates, carbon-based substrates, metal substrates, traditional paper substrates, sponge-type substrates, and cable-type substrates, can also be used as substrates of the flexible electrode. These substrates are very flexible and mechanically robust despite severe bending, enabling the employment of SCs in lightweight, wearable, and flexible electronic devices for extensive portable applications. Nevertheless, each type of flexible substrate has both advantages and disadvantages in terms of flexible SC application, which are listed in Table 1.

PDMS inherently has excellent ductility, flexibility, and mechanical strength. Therefore, flexible SCs based on PDMS substrates have better bending and electrochemical properties. Li et al. prepared stretchable MSCs on oxygen-plasma-treated PDMS substrates using 3D printing and unidirectional freezing, as in Figure 15a [187]. A nanocomposite ink consisting of MnONWs, MXene, C60, and AgNWs was constructed in a honeycomb-like porous
structure. Taking advantage of the synergies between the electrode architecture and nanocomponents, the 3D-printed MSC device exhibited excellent electrochemical performance.

Table 1. Comparison of various flexible substrates for the flexible SC electrodes.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Conductivity</th>
<th>Cost</th>
<th>Surface Area</th>
<th>Flexibility</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>metal substrate</td>
<td>high</td>
<td>moderate</td>
<td>low</td>
<td>high</td>
<td>high</td>
</tr>
<tr>
<td>traditional paper</td>
<td>low</td>
<td>low</td>
<td>moderate</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>carbon-based paper</td>
<td>high</td>
<td>moderate</td>
<td>moderate</td>
<td>moderate</td>
<td>low</td>
</tr>
<tr>
<td>sponge-type</td>
<td>low</td>
<td>low</td>
<td>high</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>cable-type</td>
<td>high</td>
<td>moderate</td>
<td>moderate</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>textile-type</td>
<td>low</td>
<td>low</td>
<td>high</td>
<td>high</td>
<td>low</td>
</tr>
</tbody>
</table>

Figure 15. (a) Schematic illustration of the fabrication process of intrinsically stretchable MSCs through 3D printing and unidirectional freezing. The 3D-printed thick interdigitated electrodes possess a honeycomb-like porous structure in combination with a layered cell wall architecture. Reprinted with permission from Ref. [187]. Copyright 2020 WILEY-VCH Verlag GmbH & Co., KGaA. (b) MXene slurry on an A4 sheet of printing paper with Meyer rod; the inset shows a snapshot of the progression of the coating process. (c) Foldable MXene/paper, schematic illustration of laser patterning of MXene-coated paper to fabricate interdigitated electrodes for MSCs, and fabricated MXene-based MSC device along with the crystallographic arrangement of Ti (gray color) and C (black color) atoms in MXene sheets. Reprinted with permission from Ref. [188]. Copyright 2016 WILEY-VCH Verlag GmbH & Co., KGaA. (d) Schematic representation of the synthesis of a stable SA-MXene nanocomposite. (e) Schematic representation of a solid-state MSC fabricated through the inkjet printing of SA-MXene nanocomposites. Reprinted with permission from Ref. [189]. Copyright 2019 Energy Storage Materials.
It is simpler and more economical to construct flexible electrodes based on ordinary paper. The paper contains a hierarchical arrangement of cellulose fibers and can be regarded as having a rough and porous surface texture that is conducive to ink adhesion without the need for extra treatments [190]. The paper surface provides a suitable substrate for solution-processed coatings of a variety of functional materials because of the capillary nature of fibers, functional groups, and intrinsic surface charge. Kuia et al. successfully manufactured MXene-on-paper energy storage devices using Meyer rod coating and direct laser machining (Figure 15b,e) [188]. Compared to those paper-based MSCs, the Ti₃C₂ MXene-on-paper MSC produced comparable power–energy densities. Wu et al. printed interdigitated MSC electrodes on photopaper using an inkjet printer (Figure 15d,e) [189]. Adding ascorbic acid into Ti₃C₂Tx MXenes can improve not only the dispersibility and oxidative stability but also enhance the spacing between the MXene layers, thereby facilitating the diffusion of the electrolyte ions. Furthermore, the manufactured solid-state MSCs displayed specific capacitance, superior mechanical flexibility, and cycle stability. Yang et al. deposited Ti₃C₂/CNTs sheets onto graphite paper for SC electrodes via electrophoretic deposition, as in Figure 16a [191]. The Ti₃C₂/CNTs electrode exhibited enhanced cycling stability and specific capacitance. (Figure 16b). Li et al. reported a flexible AMSC based on Ti₃C₂Tx//PPy/MnO₂ [192]. As shown in Figure 16c, the Ti₃C₂Tx nanosheets were formed on graphite paper (GP) as negative electrodes. The PPy/MnO₂ materials on the GP were prepared using the same method as the positive electrodes. An AMSC based on Ti₃C₂Tx//PPY/MnO₂ was then constructed using a PVA/H₂SO₄ electrolyte. The maximal energy density and areal capacitance can reach 6.73 µWh cm⁻² and 61.5 mF cm⁻², respectively (Figure 16d,e). In addition, the AMSC exhibited better flexibility when mechanically bent at different angles. (Figure 16f).

In summary, MXene-based films have advantages in terms of favorable metallic conductivity, high capacitance, and good flexibility, all of which are imperative for flexible energy storage devices. It is possible to assemble freestanding electrodes from the delaminated Ti₃C₂Tx without the utilization of additional current collectors, polymer binders, or conductive agents. However, a significant problem associated with thin-film electrode fabrication is self-restacking for MXene nanosheets because of the van der Waals interaction between the layers, which interferes with the ability of electrolyte ions to reach the active materials, resulting in poor rate performance and sluggish redox reactions. Thus, different interlayer spacers have been introduced between Ti₃C₂Tx sheets in order to alleviate the stacking problem and improve the electrochemical performance of the electrodes. The methods for preparing composite electrode materials consisting of carbon materials and MXenes include the in situ growth method, the self-assembly method, and the layer-by-layer assembly method. As a result of the increased interlayer spacing and surface area, these composite electrodes exhibit higher mechanical and electrochemical properties than pure Ti₃C₂Tx electrodes. In addition, there is a strong bonding interaction between groups terminated on the surfaces of different materials, which leads to a good degree of flexibility. However, a large number of insulating groups may adversely affect the electrical conductivity of composite materials. Ti₃C₂Tx/polymer composites are primarily produced by polymerizing polymer monomers onto the surface of Ti₃C₂Tx nanosheets. The electrodes have excellent capacitance and outstanding mechanical strength due to the superior pseudocapacitive behavior and flexibility of the polymer. Furthermore, as a result of the excellent cycling stability of Ti₃C₂Tx MXene, they also have a respectable cycle life. When combined with transition metal compounds, Ti₃C₂Tx MXene can also effectively improve electrochemical performance. On the one hand, the superior electrical conductivity of Ti₃C₂Tx MXene can substantially facilitate electron transport. On the other hand, the theoretical capacitance of transition metal compounds is relatively high, which can greatly facilitate pseudocapacitance. However, as a result of stiffness and the poor flexibility of these transition metal compounds, a majority of Ti₃C₂Tx/transition metal compound composites still exhibit low mechanical strength. For the development of lightweight and flexible MXene-based films, rational methods must be developed for constructing efficient channels to facilitate ion...
transport. The electrochemical performance of flexible Ti$_3$C$_2$Tx-based composite SCs is summarized in Tables 2 and 3.

![Schematic diagram of the preparation route of electrode films using the EPD method.](image)

(b) The plots of the specific capacitance of the three electrodes after 10,000 GCD cycles at 5 A g$^{-1}$. Reprinted with permission from Ref. [191]. Copyright 2018 Journal of Electroanalytical Chemistry.

(e) The schematic representation of the fabrication route of the flexible Ti$_3$C$_2$Tx//PPy/MnO$_2$-based AMSC. (d) The ACs of the Ti$_3$C$_2$Tx//PPy/MnO$_2$-based AMSC at 2–300 mV s$^{-1}$. (e) A Ragone plot of Ti$_3$C$_2$Tx//PPy/MnO$_2$-based AMSC compared to previously reported MSCs. (f) The CV curves of the AMSC under 0–180° bending conditions at 10 mV s$^{-1}$. Reprinted with permission from Ref. [192]. Copyright 2020 WILEY-VCH Verlag GmbH & Co., KG.

### Table 2. Comparison of the electrochemical performance of MXene-based flexible SCs.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Capacitance</th>
<th>Stability</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_3$C$_2$Tx films</td>
<td>1 M H$_2$SO$_4$</td>
<td>245 F g$^{-1}$ at 2 mV s$^{-1}$</td>
<td>100% after 10,000 cycles</td>
<td>[77]</td>
<td></td>
</tr>
<tr>
<td>ak-Ti$_3$C$_2$Tx film-A</td>
<td>1 M H$_2$SO$_4$</td>
<td>294 F g$^{-1}$ at 1 A g$^{-1}$</td>
<td>91% after 4000 cycles</td>
<td>[106]</td>
<td></td>
</tr>
<tr>
<td>d-Ti$_3$C$_2$ films</td>
<td>1 M Li$_2$SO$_4$</td>
<td>633 F cm$^{-2}$ at 2 mV s$^{-1}$</td>
<td>95.3% after 10,000 cycles</td>
<td>[107]</td>
<td></td>
</tr>
<tr>
<td>200-Ti$_3$C$_2$Tx film</td>
<td>1 M H$_2$SO$_4$</td>
<td>429 F g$^{-1}$ at 1 A g$^{-1}$</td>
<td>89% after 5000 cycles</td>
<td>[109]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx film</td>
<td>1 M H$_2$SO$_4$</td>
<td>223 F g$^{-1}$ at 0.5 A g$^{-1}$</td>
<td>93% after 1000 cycles</td>
<td>[110]</td>
<td></td>
</tr>
<tr>
<td>f-MXene-10 film</td>
<td>3 M H$_2$SO$_4$</td>
<td>83 F g$^{-1}$ at 1 A g$^{-1}$</td>
<td>89.3% after 1000 cycles</td>
<td>[113]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx-Li film</td>
<td>1 M H$_2$SO$_4$</td>
<td>892 F cm$^{-2}$ at 2 mV s$^{-1}$</td>
<td>100% after 10,000 cycles</td>
<td>[193]</td>
<td></td>
</tr>
<tr>
<td>MXene/rHGO</td>
<td>3 M H$_2$SO$_4$</td>
<td>1445 F cm$^{-2}$ at 2 mV s$^{-1}$</td>
<td>93% after 10,000 cycles</td>
<td>[128]</td>
<td></td>
</tr>
<tr>
<td>MXene/rGO-5 wt%</td>
<td>1 M KCl</td>
<td>1040 F cm$^{-3}$ at 2 mV s$^{-1}$</td>
<td>100% after 20,000 cycles</td>
<td>[130]</td>
<td></td>
</tr>
<tr>
<td>MXene/rGO-20 film</td>
<td>3 M H$_2$SO$_4$</td>
<td>300.4 F g$^{-1}$ at 2 A g$^{-1}$</td>
<td>90.7% after 40,000 cycles</td>
<td>[132]</td>
<td></td>
</tr>
<tr>
<td>MXene/graphene</td>
<td>3 M H$_2$SO$_4$</td>
<td>127 F g$^{-1}$ at 2 mV s$^{-1}$</td>
<td>95.7% after 10,000 cycles</td>
<td>[133]</td>
<td></td>
</tr>
</tbody>
</table>
### Table 2. Cont.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Electrode</th>
<th>Electrolyte</th>
<th>Capacitance</th>
<th>Stability</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_3$C$_2$T$_x$/CNT films</td>
<td>1 M KOH</td>
<td>314 F cm$^{-2}$ at 2 mV s$^{-1}$</td>
<td>95% after 10,000 cycles</td>
<td>[137]</td>
<td></td>
</tr>
<tr>
<td>MXene/CNT paper</td>
<td>1M MgSO$_4$</td>
<td>390 F cm$^{-2}$ at 2 mV s$^{-1}$</td>
<td>100% after 10,000 cycles</td>
<td>[142]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$T$_x$/CNTs film</td>
<td>3 M H$_2$SO$_4$</td>
<td>74.1 F g$^{-1}$ at 5 mV s$^{-1}$</td>
<td>86.3% after 10,000 cycles</td>
<td>[144]</td>
<td></td>
</tr>
<tr>
<td>MXene/CNT-5%</td>
<td>1 M H$_2$SO$_4$</td>
<td>300 F g$^{-1}$ at 1 A g$^{-1}$</td>
<td>92% after 10,000 cycles</td>
<td>[194]</td>
<td></td>
</tr>
<tr>
<td>Layered Ti$_3$C$_2$/PPy</td>
<td>PVA/H$_2$SO$_4$</td>
<td>35.6 mF cm$^{-2}$ at 0.3 mA cm$^{-2}$</td>
<td>100% after 10,000 cycles</td>
<td>[146]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$T$_x$/PDT</td>
<td>PVA/H$_2$SO$_4$</td>
<td>52.4 mF cm$^{-2}$ at 0.1 mA cm$^{-2}$</td>
<td>excellent cycling stability</td>
<td>[147]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/PVA film</td>
<td>1 M KOH</td>
<td>528 F cm$^{-3}$ at 2 mV s$^{-1}$</td>
<td>92% after 25,000 cycles</td>
<td>[149]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$T$_x$/PPy</td>
<td>1 M H$_2$SO$_4$</td>
<td>1000 F cm$^{-3}$ at 5 mV s$^{-1}$</td>
<td>71.4% after 4000 cycles</td>
<td>[150]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$T$_x$/PANI</td>
<td>1 M H$_2$SO$_4$</td>
<td>272.5 F g$^{-1}$ at 1 A g$^{-1}$</td>
<td>80% after 10,000 cycles</td>
<td>[151]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$T$_x$/PEDOT:PSS</td>
<td>1 M H$_2$SO$_4$</td>
<td>1065 F cm$^{-3}$ at 2 mV s$^{-1}$</td>
<td>90% after 5000 cycles</td>
<td>[164]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$T$_x$/MnO$_2$ = 6</td>
<td>1 M Li$_2$SO$_4$</td>
<td>205 mF cm$^{-2}$ at 0.2 mA cm$^{-2}$</td>
<td>100% after 10,000 cycles</td>
<td>[158]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$/MnO$_x$</td>
<td>1 M Li$_2$SO$_4$</td>
<td>392.9 F cm$^{-3}$ at 2 mV s$^{-1}$</td>
<td>89.8% after 10,000 cycles</td>
<td>[162]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$/FeOOH QDs</td>
<td>1 M Li$_2$SO$_4$</td>
<td>115 mF cm$^{-2}$ at 2 mA cm$^{-2}$</td>
<td>82% after 3000 cycles</td>
<td>[163]</td>
<td></td>
</tr>
<tr>
<td>MXene/MoO$_3$</td>
<td>1 M H$_2$SO$_4$</td>
<td>396 F cm$^{-3}$ at 10 mV s$^{-1}$</td>
<td>90% after 5000 cycles</td>
<td>[164]</td>
<td></td>
</tr>
<tr>
<td>MXene/Fe (OH)$_3$</td>
<td>3 M H$_2$SO$_4$</td>
<td>1142 F cm$^{-3}$ at 0.5 A g$^{-1}$</td>
<td>92% after 1000 cycles</td>
<td>[195]</td>
<td></td>
</tr>
</tbody>
</table>

### Table 3. Comparison of the energy density and power density of MXene-based flexible SCs.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Electrode</th>
<th>Energy Density</th>
<th>Power Density</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>ak-Ti$_3$C$_2$T$_x$ film-A</td>
<td>PVA</td>
<td>45.2 Wh L$^{-1}$</td>
<td>326 W L$^{-1}$</td>
<td>[106]</td>
</tr>
<tr>
<td>d-Ti$_3$C$_2$ films</td>
<td>PVA</td>
<td>41 Wh L$^{-1}$</td>
<td>107</td>
<td>[107]</td>
</tr>
<tr>
<td>200-Ti$_3$C$_2$T$_x$ film</td>
<td>PVA</td>
<td>29.2 Wh kg$^{-1}$</td>
<td>109</td>
<td>[109]</td>
</tr>
<tr>
<td>Ti$_3$C$_2$T$_x$ film</td>
<td>PVA</td>
<td>15.2 Wh L$^{-1}$</td>
<td>204.8 W L$^{-1}$</td>
<td>[110]</td>
</tr>
<tr>
<td>f-MXene-10 film</td>
<td>PVA</td>
<td>6.1 Wh Kg$^{-1}$</td>
<td>175.0 W Kg$^{-1}$</td>
<td>[113]</td>
</tr>
<tr>
<td>MXene/rGO</td>
<td>PVA</td>
<td>11.5 Wh Kg$^{-1}$</td>
<td>62.4 W Kg$^{-1}$</td>
<td>[128]</td>
</tr>
<tr>
<td>MXene/rGO-5 wt%</td>
<td>PVA</td>
<td>32.6 Wh L$^{-1}$</td>
<td>74.4 kW L$^{-1}$</td>
<td>[130]</td>
</tr>
<tr>
<td>MXene/graphene</td>
<td>PVA</td>
<td>50.8 Wh Kg$^{-1}$</td>
<td>215 W kg$^{-1}$</td>
<td>[133]</td>
</tr>
<tr>
<td>No</td>
<td>Ti$_3$C$_2$T$_x$/CNTs film</td>
<td>23.9 Wh kg$^{-1}$</td>
<td>498.6 W kg$^{-1}$</td>
<td>[144]</td>
</tr>
<tr>
<td>Ti$_3$C$_2$T$_x$/PEDOT:PSS</td>
<td>59 Wh kg$^{-1}$</td>
<td>9.6 kW kg$^{-1}$</td>
<td>[145]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$T$_x$/PANI</td>
<td>31.18 Wh kg$^{-1}$</td>
<td>1079.3 W kg$^{-1}$</td>
<td>[150]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$T$_x$/PEDOT:PSS</td>
<td>23 mWh cm$^{-3}$</td>
<td>7659 mW cm$^{-3}$</td>
<td>[151]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$T$_x$/MnO$_2$ = 6</td>
<td>56.94 mWh cm$^{-3}$</td>
<td>0.5 W cm$^{-3}$</td>
<td>[158]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$/MoO$_x$</td>
<td>13.64 mWh cm$^{-3}$</td>
<td>3755.61 mW cm$^{-3}$</td>
<td>[162]</td>
<td></td>
</tr>
<tr>
<td>Ti$_3$C$_2$/FeOOH QDs</td>
<td>40 mWh cm$^{-2}$</td>
<td>8.2 mW cm$^{-2}$</td>
<td>[163]</td>
<td></td>
</tr>
<tr>
<td>MXene/MoO$_3$</td>
<td>13.4 Wh kg$^{-1}$</td>
<td>534.6 W kg$^{-1}$</td>
<td>[164]</td>
<td></td>
</tr>
<tr>
<td>MXene/Fe (OH)$_3$</td>
<td>PVA</td>
<td>20.7 Wh L$^{-1}$</td>
<td>184.8 W L$^{-1}$</td>
<td>[195]</td>
</tr>
</tbody>
</table>
Table 3. Cont.

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Electrode</th>
<th>Energy Density</th>
<th>Power Density</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>Mo_{1.33}C MXene/PEDOT:PSS</td>
<td>24.72 mW h cm^{-3}</td>
<td>19.470 mW cm^{-3}</td>
<td>[167]</td>
</tr>
<tr>
<td></td>
<td>Ti_{3}C_{2}Tx films</td>
<td>0.05 μW h cm^{-2}</td>
<td>2.4 μW cm^{-2}</td>
<td>[168]</td>
</tr>
<tr>
<td></td>
<td>Ti_{3}C_{2}Tx/MnO_{2}</td>
<td>0.7 mW h cm^{-2}</td>
<td>80.0 mW cm^{-2}</td>
<td>[169]</td>
</tr>
<tr>
<td></td>
<td>Ti_{3}C_{2}Tx/rGO</td>
<td>8.6 mW h cm^{-3}</td>
<td>0.2 W cm^{-3}</td>
<td>[177]</td>
</tr>
<tr>
<td></td>
<td>Ti_{3}C_{2}Tx</td>
<td>43.5 mW h cm^{-2}</td>
<td>87.5 mW cm^{-2}</td>
<td>[170]</td>
</tr>
<tr>
<td></td>
<td>MXene</td>
<td>19.2 mW h cm^{-3}</td>
<td>14 W cm^{-3}</td>
<td>[178]</td>
</tr>
<tr>
<td>Fiber</td>
<td>TiC nanowires</td>
<td>13.1 Wh kg^{-1}</td>
<td>20.2 kW kg^{-1}</td>
<td>[179]</td>
</tr>
<tr>
<td></td>
<td>MXene/PPy</td>
<td>1.30 mW h g^{-1}</td>
<td>41.1 mW g^{-1}</td>
<td>[184]</td>
</tr>
<tr>
<td></td>
<td>MXene/MWCNTs</td>
<td>22.11 mW h cm^{-3}</td>
<td>2.99 W cm^{-3}</td>
<td>[185]</td>
</tr>
<tr>
<td></td>
<td>PPy/MXene/PMFF</td>
<td>29.2 μW h cm^{-2}</td>
<td>25 mW cm^{-2}</td>
<td>[186]</td>
</tr>
<tr>
<td>PDMS</td>
<td>MXene-AgNW-MnONW-C60</td>
<td>19.2 μW h cm^{-2}</td>
<td>58.3 mW cm^{-2}</td>
<td>[187]</td>
</tr>
<tr>
<td>Paper</td>
<td>MXene</td>
<td>0.77 μW h cm^{-2}</td>
<td>46.6 mW cm^{-2}</td>
<td>[188]</td>
</tr>
<tr>
<td></td>
<td>sodium ascorbate-MXene</td>
<td>100.2 mW h cm^{-3}</td>
<td>1.9 W cm^{-3}</td>
<td>[189]</td>
</tr>
<tr>
<td>GP</td>
<td>Ti_{3}C_{2}CNTs</td>
<td>0.56 Wh kg^{-1}</td>
<td>416.7 W kg^{-1}</td>
<td>[191]</td>
</tr>
<tr>
<td></td>
<td>Ti_{3}C_{2}Tx/PPy/MnO_{2}</td>
<td>6.73 μW h cm^{-2}</td>
<td>204 μW cm^{-2}</td>
<td>[192]</td>
</tr>
</tbody>
</table>

4. Conclusions and Perspectives

In summary, this review article detailed recent advancements in the development of flexible electrodes based on MXenes for applications in SCs. A concise introduction of MXenes as emerging 2D materials was provided, along with the different synthesis methods of Ti_{3}C_{2}Tx MXene and its influence on its electrochemical properties. The applications of MXene-based flexible electrodes in SCs, according to the different construction methods of flexible electrodes based on MXenes and their composite electrodes, which are the theme of this review, were also presented. Different construction methods such as self-supporting, PET-supported, fabric fiber-supported, and other substrate-supported MXene-based films as flexible electrodes for fSCs were discussed in detail. In recent years, researchers have achieved substantial advances in the study of MXene-based SCs, but there are still a great number of obstacles to their development. Consequently, we need to consider the following factors in subsequent research:

(1) In spite of the growing body of research on the preparation of MXenes, wet chemical etching remains the most common method for the production of MXenes. However, chemical etching usually uses corrosive solvents or gases, and etching conditions are harsh. The emission of pollutants is another problem that cannot be ignored. Additionally, MXenes are easily oxidized in humid environments, which limits not only their synthesis on a large scale but also their application areas and environmental status. The future direction of MXene synthesis should be facile, low-cost, green, and have excellent and stable properties. Lastly, surface functional groups have a considerable impact on their physicochemical properties, and the specific capacitance of Ti_{3}C_{2}Tx is far from optimal, so it is still possible to improve the design and control of surface functional groups during the etching process.

(2) Due to the 2D lamellar structure, hydrophilic surface, and excellent metallic conductivity of MXenes, they are preferable as energy storage electrode materials. What’s more, MXenes can achieve high volumetric capacitance due to impressive density and pseudocapacitive behavior. These properties make MXene very appealing for flexible SCs. However, the gravimetric capacitance of MXene flexible electrodes has yet to be further improved because of the aggregation and restacking of MXene nanosheets. On the one hand, the stacking of MXene lamellar structures can be prevented by loading small-sized pseudocapacitance materials such as nanodots. On the other hand, the density and additional pseudocapacitance can be increased by anchoring nanodots to pseudocapacitive material on MXene nanosheets so as to improve the mass-specific capacity and electrochemical performance.
Along with the proliferation of emerging smart wearable electronic devices (SWEDs), there has also been an increase in the demand for flexible SCs to be integrated with other flexible devices or wearable devices to provide them with a power source or additional functions. For example, integration with sensors or environmental monitoring equipment can allow them to operate independently and work under special conditions. A self-powered integrated system composed of strain sensors and flexible SCs is capable of detecting stable human motion with precision, which makes smart flexible SCs more suitable for SWEDs. In recent years, research on self-repairing, self-charging, and electrochromic flexible SCs has also become one of the new research hotspots and development trends. In addition to traditional electrochemical properties, such as specific capacity and cyclic stability, we should also pay more attention to the photosensitivity, self-healing, transparency, and other properties of intelligent electrode materials. In conclusion, it is imperative to design novel fSCs with intelligent and interactive characteristics.

It is crucial to employ solid or gel electrolytes with high conductivity and efficient infiltration because flexible SCs frequently need to work in a curved or bending state, which increases the risk of electrolyte leakage. Ionic liquid-based gel (ionogel) electrolytes have been demonstrated to have better thermal stability, chemical inertness, as well as non-flammability. In addition to this, ionogel electrolytes also have the characteristics of the ionic liquid itself, with a wide electrochemical potential window, high ionic conductivity, and negligible vapor pressure, making them a promising electrolyte choice for the production of all-solid flexible SCs with high energy density. However, the use of ionogel electrolytes is still limited by the low capacitance and slow speed of ion transport. Thus, more efforts have been made toward improving the ionic conductivity of ionogel electrolytes and expanding the voltage window of Ti$_3$C$_2$Tx electrodes in aqueous electrolytes.

In addition, the design of the flexible current collector is important, as it is a crucial component of the electrode. The conventional current collectors, such as carbon-based, planar metal-based, and 3D metal-based, increase the whole mass of the supercapacitor and thus reduce the energy density. Therefore, considerable attempts and methods should be made to develop ultrathin 3D (to load more active materials) metallic current collectors. The manufacturing cost of flexible supercapacitors can also be reduced if components such as current collectors, adhesives, and encapsulation films are used as little as possible under the premise of ensuring performance stability. As a consequence, using self-supporting MXene film as a flexible electrode without current collectors is also a development direction for future flexible SCs.

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