MXenes for Non-Lithium-Ion (Na, K, Ca, Mg, and Al) Batteries and Supercapacitors

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1. Introduction

Lithium-ion battery (LIB) is one of the top significant energy storage technology, which is widely used in convenient electronic gadgets and control electric vehicles.[1] In 2019, the Nobel Prize for chemistry was awarded to Prof. John B. Goodenough for the development of rechargeable LIBs. The lightweight, rechargeable and powerful LIB is now used in everything from mobile phones to laptops and electric cars. It can also store much energy from solar and wind energy, making it possible for a fossil-fuel-free society. LIBs are being used around the world to power our portable electronic devices for communication, work, learning, and searching for knowledge. Moreover, they make it possible to develop long-distance electric vehicles and store renewable energy such as solar energy and wind energy, which further promotes collaborative innovation in the field of new energy storage. Thus, how to develop electrode materials with high capacity, high energy density, and long life is the key challenge to realize high-performance energy storage devices. In any case, the vast scale of electrical energy storage utilization of LIBs is hampered by uncertainties of restricted lithium supplies, high manufacturing cost, and security issues.[2,3] In such a manner, the advancement of new battery technologies is direly required for the up and coming age of sustainable power source advances. As of now, Na+,[4,5] K+,[6,7] Mg2+,[8–11] Ca2+,[12,13] and Al3+.[14,15] batteries are pulling in much consideration because they utilize plenteous elements, significant theoretical capacities, appropriate potential (negative redox), operational comfort, and environment-friendly nature.

Compared with lithium-ion batteries, the electrochemical performance of non-lithium-ion batteries (NLIBs) depends largely on its cathode structure and electrolyte properties. At present, the research of NLIBs mainly focuses on the preparation of appropriate cathode materials. Various materials with enormous interstitial spaces, including layered TMO,[12] olivine FePO4,[16] and Prussian blue frameworks,[17] have been investigated to show higher capacities and cyclabilities as cathodes. In contrast, with the rapid development of cathode materials, the development of anode materials is much slower, limited to carbon-related materials and IVA, VA group metal compounds.[18–25] Amazingly, the vast majority of these materials do not work for NLIBs. For example, graphite, the utmost generally utilized anode material in LIBs, shows first-rate cyclabilities at a small electrode materials[18–20] show first-rate cyclabilities at a small current density with a capacity not higher than 300 mAh g⁻¹. However, metal composites exhibit high electrochemical
properties at the expense of large volume changes,[21–25] which leads to capacity attenuation and anode structure destruction during the cycle. Therefore, it is an inevitable trend for NLIBs to develop anode materials with high reversibility, rapid intercalation/deintercalation, and excellent electrochemical performance.

Layered and 2D materials, for example, graphene and the metal chalcogenides, are potential host materials for LIBs with high capacities due to their exposed and unique morphologies.[27–34] After 2012, a kind of material began to be concerned, that is MXene material. This is a 2D layered metal carbide and metal nitride material. This is a new area of interest for energy storage researchers.[35–37] MXenes are generally synthesized by the etching of A element from the MAX phase (the general formula of MAX is $M_{y+1}AX_y$ ($y = 1$–3)), where A is the element of group IIIA or IVA and X is a carbon or nitrogen. For clarity, Figure 1a highlights the constituent elements. In recent years, a large number of MXene have been found and used as electrode materials for energy storage system. Due to the excellent physical and chemical properties of MXene, the number of publications is increasing every year, as shown in Figure 1b. Due to the etching of MAX phase in acidic aqueous solution, the surface terminals of MXene 2D films are mainly functionalized by HO–, O–, S–, and F–. MXenes materials are good conductors of electricity,[35,36,38] and have many applications such as gas storage,[39] photocatalyst,[40] thermoelectric,[41] and display clear vitality as energy storage materials.[42–47] In recent years, Ti$_3$C$_2$Tx MXene has also been used as a precursor for the preparation of Ti-based chalcogenides, such as TiS$_2$/C$_{pvp}$[48] TiO$_2$/C,[46] NaTi$_{1.5}$O$_{8.3}$,[50] and K$_2$Ti$_4$O$_9$.[56] Most of these MXene-derives are used as electrode materials in energy storage technologies and reveals excellent electrochemical properties. Using TiS$_2$/C$_{pvp}$ and NaTi$_{1.5}$O$_{8.3}$ as sodium storage electrodes, TiO$_2$/C and K$_2$Ti$_4$O$_9$ as potassium storage electrodes, they have high reversible capacity, excellent rate performance and ideal energy density. Note that all of these have excellent electrochemical properties because they have the appropriate interlayer spacing to intercalate Na$^+$ and K$^+$. Besides, experimentally MXenes display high lithium storage capacity as 410 mAh g$^{-1}$ and excellent rate capabilities.[42] The adsorption spectra and theoretical calculation results show that MXene can promote the intercalation of Li$^+$ in 2D layers. Li$^+$ intercalation is improved when the HO– surface terminal is transformed into O– terminal by high temperature annealing or metal reduction method.[45,53] The high capacity of lithium may be due to its unique multilayer adsorption of Li-ions.[45] More interestingly, when MXene electrodes are used as electrochemical capacitors rather than graphite, different metal ions including Na, K, Mg, and Al ions can be inserted into the 2D layers of MXene.[43] Thus, this unlocks the new platform to utilize MXenes as electrode (anode) materials for NLIBs. Furthermore, although the non-terminated MXene known as bare MXene is anticipated to have appealing physical properties,[31,39,47] but there is no exploratory or theoretical research to explore the best way to synthesize non-terminated MXene from the functional MXene. Therefore, it is also necessary to study the potential technology of synthesizing non-terminated bare MXenes. In this paper, the research progress of MXene and its application as electrochemical energy storage materials in recent years is reviewed. The emphasis is to realize the intercalation of metal ions (Na, Ca, K, Mg, and Al-ion) in the 2D MXene electrode.

It is anticipated that, both O-functionalized and non-terminated (bare) MXenes are suitable electrode materials as an anode for NLIBs.[52] Specifically, non-terminated (bare) MXenes display excellent capacities and capabilities over O-functionalized ones.[52] The studies show that Na-ions and K-ions exhibit reversible reactions with functionalized MXene electrode, which is reliable with computational calculations. In addition, Mg and Al show particularly high theoretical capacities because of the stable multilayer adsorption mechanism.[42]

In this review, the ongoing advances in MXene-based materials for non-lithium-ion energy storage technologies are illustrated. The preparation strategies and structural properties of
MXenes are briefly abridged. Afterward, the emphasis is placed on the applications of MXene-based materials for various energy storage gadgets, especially NLIBs, including sodium-ion batteries (SIBs), potassium-ion batteries (PIBs), calcium-ion batteries (CIBs), magnesium-ion batteries (MIBs), aluminum-ion batteries (AIBs), and supercapacitors (SCs). Their energy storage-related properties, for example, composition, structure, termination, electronic, and mechanical properties, are also discussed. At last, in this review article, we also highlight the present issues, openings, and future problems of MXene-based electrode materials. It is expected that extensive research on MXene will promote further improvement of attractive 2D MXene energy storage technology shown in Figure 1b.

2. Synthesis Approaches

Due to the partiality of the 2D nanochips, the research on the preparation of 2D MXene with high quality and high structure dignity is still in the exploratory stage. In brief, two important methods for the preparation of 2D MXene are proposed: top-down preparation and bottom-up preparation. In the former synthesis method, the bulk material is peeled off into few layers and the latter method is the contrary of the former, in which the material develops at the atomic or molecular level. For an illustration of the bottom-up preparation strategy, the excellent quality 2D Mo2C with the thickness in nanometers and cross-sectional length in μm were synthesized by the chemical vapor deposition method (CVD). This strategy harvests MXenes with some defects and large cross-sectional size layers, and encourages the study of its inherent characteristics. For the top-down method, MXene is synthesized by etching a certain layer from its layered MAX phase. In order to illustrate, in the early stage, MXene (Ti3C2Tx) was prepared by etching Al layer with HF aqueous solution of the MAX phase (Ti3AlC2) to prepare. The MAX phase material is generally synthesized by a simple route of roasting a preball blend processed of TiC and Ti2AlC at a temperature of more than 1200 °C in a defensive environment. Due to different combination conditions, the MAX phase has different morphology and size, which may assume a fundamental job in deciding the nature of the Ti3C2Tx materials. Until the date, much exertion has been directed toward the investigation of novel strategies to synthesize Ti3C2Tx, and different etchants (e.g., NH4HF2, LiF, NaF, KF, NH4F, and acids) have been used. In this review, we mainly discuss the wet techniques of etching synthesis MXenes.
2.1. HF Based Etching

The precursor of MXene is the MAX phase, which is a kind of ternary layered material with excellent ceramic and metal properties. Like ceramics, it has a high modulus of elasticity, low density, good thermal stability, and oxidation resistance. Like metals, it has excellent heat transfer and conductivity as well as low hardness. It can be forged like metals and graphite, can be processed at high temperatures and has good plasticity and self-lubricating properties. For illustration, M–X bond is a strong bond due to its covalent and ionic bond properties, which is why the MAX phase has good acid/Alkali corrosion resistance. On the other hand, the M–A bond and A–A bond have more metal bond characteristics, and the bond is relatively weak, so the atomic reaction activity of a layer is the highest. Xie et al.[53] reported that the chemical activity of the MAX phase strongly depends on the chemical activity of atoms, and decreases with the increase of MX layer thickness.

In addition, at high temperature, an atom diffuses away from the M_{n+1}AX_{n} matrix, leading to partial decomposition of the MAX phase. Therefore, M_{n+1}X_{n} can be obtained by selective etching of A-layer in MAX phase. Although the metal bond is weaker than the MX bond, its binding force is still strong. Therefore, MXene cannot be prepared by the micromechanical stripping method, but only by chemical liquid etching method of the MAX phase. On this basis, Naguib et al. prepared 2D MXene crystals by acid etching in 2011.[35] Taking the MAX phase of aluminum (Al) as an example, the reaction with HF to generate 2D MXene can be divided into two steps. For example, in Equation (1), the Al element with the MAX phase reacts with HF to generate AlF3 and H2. The MAX phase is dissociated into 2D MX, which exists in HF aqueous solution

\[ M_{n+1}AlX_{n} + 3HF \rightarrow AlF_{3} + M_{n+1}X_{n} + 1.5H_{2} \]  

(1)

In the second step, the newly formed M_{n+1}X_{n} has very high surface activity. In order to balance the valence state, the outer layer M-ion reacts with surrounding H2O or HF to generate 2D M_{n+1}X_{n}(OH)_{3} (Equation (2)) or M_{n+1}XF_{2} (Equation (3)) with F− or HO− termination groups. It is noted that the Equations (2) and (3) occurred side by side

\[ M_{n+1}X_{n} + 2H_{2}O \rightarrow M_{n+1}X_{n}(OH)_{3} + H_{2} \]  

(2)

\[ M_{n+1}X_{n} + 2HF \rightarrow M_{n+1}X_{n}F_{2} + H_{2} \]  

(3)

However, only MXene with F−, HO−, and other functional groups on its surface can be obtained by chemical liquid phase corrosion, but pure MXene cannot be obtained, which may lead to changes in the performance of MXene. Moreover, the concentration and reaction time of the chemical etching play a decisive role in the experimental results. If the reaction time is too short or the concentration of the etchant is too low, MXene may not be prepared; if the concentration of the etchant is too high, MAX maybe completely dissolved. For example, Srivastava et al.[54] treated Ti3AlC2 with 18% HF to obtain a nanosheets of Ti3C2 (Figure 2a). When they applied different temperatures during the etching process, they obtained different interlayer spaces, as shown in Figure 2b.

How to prepare nonterminated Mxene, i.e., bare MXene is still a crucial problem to be solved. Along these lines, there are many different kinds of MXenes such as TiNbCTx,[36] Ti2CTx,[46] Ti3CN2Tx,[36] Ta2CTx,[36] Nb5CTx,[36] V2CTx,[69] Nb3Ti2O3CTx, Mo2CTx,[59,61] Zr2CTx,[62] (Nb6Ti2O3)2CTx,[63] Nb2CTx,[64] and Hf2CTx,[64] have been effectively synthesized by different researchers using HF as an etchant to remove a certain layer of atoms from precursors. Among all, Mo2C carbide is the special and first one, which was synthesized by the etching of Mo2GaC rather than a MAX one. Also, Zr2C is a type of MXene synthesized from Zr1Al2C6, it is not an ordinary MAX phase, it is a ternary or quaternary metal carbide/nitride with typical number of layers and having general formula of M_{n+1}Al_{n+1}C_{m+2}.[65] Beside, these ternary or quaternary metal carbides/nitrides a research group Anasori et al.[55] predicted dual metal carbides/nitrides (M′M″Xene) using computational studies and synthesized some dual metal MXenes experimentally such as Mo2TiC2Tx, Cr2TiC2Tx, and Mo2Ti2C3Tx, they also used HF solution as an etchant (Figure 2c–e).

2.2. Fluoride Salt-Based Etching

Although HF etching has been widely used in the synthesis of MXene and achieved many successes, this method needs to be treated with toxic HF, which is an obstacle for handy application.[55,61,66–68] Therefore, researchers are committed to looking for milder and safer etchants. Halim et al.[69] proposed that NH4HF2 as a new type of fluoride salt-based etchant. Because NH3 and NH4+ are intercalated into MXene layers, the lattice parameters of MXene layers are 25% higher than those of HF etched. Ghidiu et al.[70] reported the use of a mixture of LiF and HCl as an etchant rather than toxic HF. The in-situ produced HF can etch the ‘A’ layer instantly and selectively, which is a simpler, nontoxic and faster way. Due to the intercalation of water and cations between MXene sheets, MXene has large interlayer spacing and weak interactions. Compared with the flakes prepared with toxic HF, the flakes prepared with mild LiF and HCl have no nano defects. In addition, NaF, KF, CsF, and tetrabutylammonium can also replace LiF, while H2SO4 can replace HCl. Nb2CTx,[63] Ti2CTx,[63] (Nb6Zr2O3)2CTx,[63] Mo2TiC2Tx,[55] Cr2TiC2Tx,[55] and Mo2CTx,[59] were successfully prepared by this method. Liu et al.[58] reported the synthesis of Ti2CTx MXene by fluoride salt etching method and the FESEM images of as-synthesized Ti2CTx MXene are shown in Figure 2b–j. The MXene layers are effectively separated with larger interlayer spacing. Figure 2j shows that when KF+NH4F+HCl mixed salt is used at 40 °C, the interlayer spacing is larger than that synthesized with other fluoride etchants. Interestingly, the lattice parameter of MXene obtained by the HF etching is c = 20 Å, while, the lattice parameter of MXene synthesized by the salt etching is bigger as of ≈40 Å.[70] Furthermore, the synthesis of nitride MXene is still a challenge because of its low cohesive energy, low stability and stronger Al=N bond than Al–C. In 2016 Urbanowski et al.[66] proposed safer and simpler etching method toward Ti3AlN4 etching to synthesize nitride MXene, by using the molten fluoride salt mixture (LiF, KF, and NaF) in Ar atmosphere at 550 °C.
However, the XRD pattern of nitride MXene shows that its crystallinity is not as good as that of carbide MXene, which indicates that there are some complex problems in molten salt etching nitride. The researcher assumed that wet chemistry and fluoride salt-based etching processes are effective methods to synthesize MXenes, this marvel might be because of the intercalation of water or potential cationic between the negatively charged hydrophilic Ti$_3$C$_2$Tx layers. These outcomes may open another way to synthesize auspicious MXene materials. Salt-based etching is much milder than HF etching. Furthermore, the size of the flakes obtained by salt etching is larger than that obtained by HF etching. More significantly, the yield might be $\approx$100%, which is equivalent with the aqueous HF technique.$^{[35,36,71]}$ When a few flake MXene is obtained from the multilayer MXene, the mass yield value is about $\approx$45%, which is higher than the previously reported layered Ti$_3$C$_2$T$_x$. Mean-while, comparable methods using mixture of fluoride salts (e.g., NH$_4$F, KF, and NaF) and acids (e.g., HF, HCl, and H$_2$SO$_4$) as etchants are reported.$^{[58,72-74]}$ In all of these techniques, the acid and salt of fluoride react in situ to form HF. In conclusion, a large number of cations (e.g., NH$_4^+$, Al$^{3+}$, K$^+$, Ca$^{2+}$, Li$^+$, and Na$^+$) and water can be immediately inserted between the MXene layers from the solution of salt and acids, resulting in multifunctional terminated MXene with novel and developing highlights, such as extended interlayers, high electrical conductivity, large size flakes, and modified surface termination.$^{[43,70,75]}$

### 2.3. Fluorine Free Etching

Because of the destructive and harmfulness of fluoride acidic solution, many other protective and economic methods have been studied. For example, Yang et al.$^{[57]}$ reported a fluorine free electrochemical method for etching Ti$_3$AlC$_2$ in aqueous electrolyte (Figure 2g) to obtain high yield MXene-Ti$_3$C$_2$T$_x$ nanosheets. In this method, in the process of anode etching, the Cl$^-$ etched Al atomic layer and NH$_4$OH intercalation can peel out the MXene edge of anode surface. Due to the prohibition of F, the peeled Ti$_3$C$_2$T$_x$ flakes are O- and HO- terminated instead of F-terminated, displaying an astounding capacitance in SCs application. Furthermore, there is another method of fluorine-free etching. Recently, Zhang and co-workers$^{[76]}$ reported a method of synthesizing fluorine-free high-purity MXene material Ti$_3$C$_2$T$_x$ by hydrothermal alkali etching (Figure 3a). In theory, although it is generally believed that alkali can etch the Al element from Ti$_3$AlC$_2$ MAX, the existing reports can not only use alkali to achieve the preparation of high purity Ti$_3$C$_2$T$_x$, the main kinetic obstacles are the oxides and hydroxides of MXene.
Al produced in the reaction. The Bayer method, inspired by the aluminum industry, finally realized the etching of the Al element in Ti₃AlC₂ by NaOH. The purity of the product was 92 w% without the use of fluorine-containing reagent (NaOH, 27.5 m) at 270 °C hydrothermal treatment). Because the product does not contain F-terminal group, the mass specific capacitance and volumetric capacitance of the prepared Ti₃C₂Tx thin film electrode is 314 F g⁻¹ and 511 F cm⁻³ at 1 m H₂SO₄ and a scan rate of 2 mV s⁻¹, which are 214% higher than those of the multilayer Ti₃C₂Tx prepared by HF. In addition, this method can also be used to prepare new MXene materials by etching the MAX phase containing A element. The morphology of the prepared MXene is shown in Figure 3b–d.

In the above acidic and alkaline methods, the strongest HF and 27.5 m NaOH are used for etching and should be heated at high temperature under pressure, which may also have safety problems. For that reason, Cheng and co-workers[77] reported a secure organic based solvent for etching and delamination of Ti₃AlC₂. In this methodology, the tetramethylammonium hydroxide (TMAOH) was used for etching as well as for delamination (Figure 3e). There are two reasons for using TMAOH to remove the Al atomic layer: one is that TMAOH has a strong tendency to attack Al; the other is that in the etching process, Al(OH)₄⁻ and TMA⁺ are generated and inserted between Mxene layers (Figure 3f), which can cause delamination while shearing the layer. The suspension of as-synthesized Ti₃C₂ prepared in H₂O, and it shows the Tyndall effect (Figure 3g). According to the above discussion, it is noted that, distinctive surface termination of the as-synthesized Ti₃C₂ produced.

In addition to the inherent compositions, these compositions are sufficient to determine the properties of various MXenes. The synthesis strategy and the etchant selection directly affect the subsequent properties of MXenes as far as morphology, surface terminations, and the surface defects of the flakes.[78] It is worth noting that HF etching can produce particles with accordion-like morphology and small size flakes with abundant defects. Sang et al.[72] revealed that the HF concentration can control the defect distribution of synthesized MXene layers. Specifically, lower HF concentration, shorter etching time and no sonication delamination will result in lower defects, bigger flake size and lower yield of MXene, so as to obtain higher electronic conductivity. In addition, it also revealed that the defects of MXene and active cations usually leads to reactions, so the Coulombic efficiency decreases in the first cycle.[79]

Moreover, it is important to realize the risk valuation when dealing with dangerous HF.[82,83] Various etchants have been proposed to synthesize MXenes, and everyone might be reasonable for specific applications. Table 1 represents the different etching conditions and lattice change. For example, when high electrical conductivity, bigger flake size, larger interlayer spacing and mechanical properties are needed, mild etchant conditions are recommended, while HF is more suitable to obtain MXene with small flake size and abundant defects.

Therefore, structure, properties, materials, and target applications of MXene should be considered when choosing the
appropriate etching strategy. The adaptable properties of different MXene allow tuning in applications such as energy storage, assistances for composites, gas sensors and biosensors, purification of water, lubricant, photocatalysis, electrocatalysis, and electromagnetic impedance. Specifically, a large portion of the publicized MXenes has combined highlights, including high electronic conductivity, machine property and hydrophilicity, which are attractive features of electrochemical energy storage applications. To sum up, it is a better choice to prepare MXenes with high conductivity, which is suitable for energy storage technology under mild conditions.

### 3. Properties

Due to its typical structural features and composition, MXenes have multifarious mechanical and physicochemical properties. For instance, 2D Ti$_3$C$_2$T$_x$ displays remarkable electrical conductivity (as shown in Figure 4g) due to its metal properties and three layers of metal (Ti) atoms, one layer after another is embedded between two carbon atom layers. Computational studies have concluded that the mechanical, electronic and other physical and chemical properties of MXene are directly affected by the number of metal atomic layers and strain. Both molecular dynamic and computational studies predict that the toughness of M$_x$X$_3$ and M$_2$X$_2$ is smaller than that of M$_2$X MXene. However, for the measurement of mechanical properties, the MXene film will not be used as a single flake. A cylindrical MXene made of 5 μm thick Ti$_3$C$_2$T$_x$ paper can bear 4000 times of its own weight. Furthermore, if polyvinyl alcohol (PVA) is inserted in between Ti$_3$C$_2$T$_x$ layers, the MXene film will not be used as a single flake. A variety of MXene composites were synthesized by using polypyrrole polyethylene or polydimethylsiloxane (PDMS), with PVA which improved the mechanical and electrochemical properties of MXene. Because Ti$_3$C$_2$T$_x$ has the same topological structure as graphene, such as high surface area, excellent mechanical and chemical stability, excellent flexibility and electrical conductivity, Ti$_3$C$_2$T$_x$ is effectively rolled into different flexible and freestanding forms with exciting properties. Gogotsi's group has effectively prepared the conductive and flexible films of Ti$_3$C$_2$T$_x$@PVA and Ti$_3$C$_2$T$_x$@PDDA composites by vacuum filtration techniques. The composite film is very flexible and can be promptly warped to the required shape without obvious damage (Figure 4b,d).

Due to the interaction between the surface of Ti$_3$C$_2$T$_x$ layer and PVA, the mechanical properties are improved. In addition, ever more reports mentioned that Ti$_3$C$_2$T$_x$@polymer composite has good heat resistance, electrochemical property and wear resistance. In a recent report, pyrrole was mixed with Ti$_3$C$_2$T$_x$ suspension. Because of the acidity of pyrrole, MXene@polypyrrole can be polymerized without any oxidant at the initial stage, and the composite with excellent electrochemical capacitance was obtained. In addition, MXene/CNTs composites have been prepared recently for energy storage.

Similarly, the surface termination produced in the preparation process will undoubtedly contribute to the various properties of 2D Ti$_3$C$_2$T$_x$, such as electron negativity and hydrophilicity, and encourage the colloidal of MXene in the best polar solvent. In general, the preparation process has a significant impact on the quality and performance of MXenes. In the previous studies, the ultrasonic delamination yield of MXene in water was low. In any case, the multilayered Ti$_3$C$_2$T$_x$ synthesized by acid and fluoride salt etching is peeled off by ultrasound, and cation and water molecules are inserted between the multilayer Ti$_3$C$_2$T$_x$ as spacer. The popular method of delamination of MXene is to insert large molecules between layers, such as dimethyl sulfoxide (DMSO), amine and urea, and help MXene delamination under sonication. In the presence of surface terminations, layered Ti$_3$C$_2$T$_x$ nanoflakes have hydrophilicity and negative potential (~39.5 to ~63 mV) so the colloidal stability of Ti$_3$C$_2$T$_x$ in aqueous medium enables us to prepare various functional Ti$_3$C$_2$T$_x$, such as composite materials with polymers and other polar nanomaterials.

### Table 1. Experimental conditions of MXene synthesized by MAX phase and their lattice spacing.

| MXene$^{a}$ | MAX phase | Etchant | Time@Temperature of etching (h@°C) | Lattice space (nm) | Ref. |
|-------------|-----------|---------|-----------------------------------|-------------------|------|
| Ti$_3$CT$_x$ | Ti$_3$AlC | 10%, HF | 10@RT | 1.36 | 1.50 | [36] |
| Ti$_3$C$_2$T$_x$ | Ti$_3$AlC | 50%, HF | 2@RT | 1.84 | 2.05 | [36,35] |
| Mo$_3$CT$_x$ | Mo$_3$GaC | 12 m HCl+3 m LiF | 384@35 °C | – | – | [81] |
| Ti$_3$C$_2$T$_x$ | Ti$_3$AlC | 5 m LiF+6 m HCl | 40@45 °C | – | – | [70] |
| Nb$_2$CT$_x$ | Nb$_2$AlC | 50%, HF | 90@RT | 1.38 | 2.23 | [60] |
| Ti$_3$N$_2$T$_x$ | Ti$_3$AlN$_x$ | Molten LiF, NaF and KF | 0.5@550 °C | – | – | [58] |
| V$_2$CT$_x$ | V$_2$AlC | 50%, HF | 8@RT | 1.31 | 2.40 | [60] |
| Ti$_3$C$_2$ | Ti$_3$AlC | 1 m NH$_4$Cl+0.2 m TMAOH | 5@RT | – | – | [57] |
| TiN$_2$CT$_x$ | TiN$_2$AlC | 50%, HF | 28@RT | 1.38 | 1.49 | [36] |
| Ti$_3$C$_2$ | Ti$_3$AlC | 27.5 m NaOH | 12@270 °C | – | – | [78] |

$^{a}$RT for room temperature.
In recent years, Maleski et al. [93] systematically studied the dispersity of MXene nanosheets in different organic solvents (Figure 4e,f). The results show that the dispersity of Ti$_3$C$_2$T$_x$ in polar solvent is better, for example, propylene carbonate (PC), H$_2$O, N-methyl-2-pyrrolidone (NMP), N,N-dimethylformamide (DMF), ethanol, and DMSO, because of the comparable surface chemistry of solvents and MXene. However, toluene, 2-dichlorobenzene, n-hexane, and other high organic nonpolar solvents have low dispersion, which may be due to their hydrophobicity and nonpolarity (Figure 4e,f).

In addition, the surface terminals of MXene have an important impact on the electronic properties of MXene. Tang et al. [44] reported a computational study to understand the impact of surface functionalization and geometry stability after functionalization, as shown in Figure 5. In this study, three different geometries are calculated, and in I-type, the F- and HO- terminals are located in a hollow position and surrounded by three adjacent carbon atoms or directly point to the Ti atom. In type II geometry, the F- and HO- terminals are located at the top of the carbon atom, while the third type is a combination of type I and type II geometry. Type I geometry is the most favorable and stable in energy, and type II geometry is the most unstable. This structural stability indicates that F- and HO- tend to attach to the hollow site (I-type) and the lowest stability of type II is probably due to the steric effect between the terminal and the carbon atom. Carbon, on the other hand, can provide electrons for terminals.

Based on the above discussion, the physicochemical properties and surface structural properties of MXenes have been studied experimentally and computationally in recent years. All the while, MXene’s research and properties, including electronics, dielectric, magnetic, optical, oxidation, catalysis, and electrochemical properties, have been widely used in various fields. As follows, the most appealing properties in related energy storage applications are mechanical, electronic, and electrochemical properties.

4. Energy Storage Applications

Energy storage device is an important material basis of modern human life. The development of reliable and environmentally-friendly energy storage devices is one of the important challenges facing mankind in the 21st century. Among all kinds of energy storage technologies, electrochemical energy storage technology plays an important role in the rapid development of portable electronic equipment and electric vehicles, and the performance requirements of energy storage devices are higher and higher. There is no doubt that the performance of energy storage devices depends on the development and utilization of energy storage materials. In general, the requirements for energy storage materials are as follows: 1) reversible redox reaction; 2) easy access to electrolyte ions; 3) many redox sites;
as possible; 4) good electrical conductivity. In recent years, 2D materials have shown great advantages in the field of energy storage due to their large specific surface area and short ion transport path. The 2D materials have only atomic layer thickness, many surface active sites and excellent mechanical properties, which meet the requirements of energy storage devices. At present, electrochemical energy storage devices mainly include secondary batteries and supercapacitors. Due to its unique 2D structure, high conductivity, high ion diffusion, and other advantages, in recent years, more than 20 kinds of MXene materials have been successfully prepared and many important breakthroughs have been made in the field of energy storage. Due to the 2D characteristics and excellent conductivity of MXene materials, they show excellent performance in electrochemical energy storage devices such as batteries or supercapacitors. Therefore, it is urgent to summarize the progress of MXene synthesis and its new application in the field of energy storage, especially for non-lithium energy storage technologies.

4.1. Sodium-Ion Storage

Sodium-ion batteries are going to promising energy storage for a large scale because of abundance and low cost as compared to lithium.[111–120] However, due to the large size of Na+, the diffusion of Na+ in electrode materials needs to be improved. A prevailing strategy is to synthesize nanomaterials as a cathode material for SIBs with excellent performance.[121–123] The time for the diffusion of Na+ will be drastically reduced by lessening the pathways for Na+ intercalation/deintercalation. Additionally, the diffusion of Na+ can also be moderately influenced by escalating electronic conductivity. Consequently, MXene and its composites have been accounted for as superb electrode materials for SIBs,[124–129] because MXenes can intercalate different ions with various sizes. This valuable feature of MXene is sufficient for the construction of SIBs. Furthermore, it is anticipated that the double metal ion layer would prompt twofold the capacity. Besides, from the point of view of surface tunability and structural changeability, many different MXenes can give a wide range of working potentials, which makes them suitable as either anodes or cathodes.[111,112] The insertion and deinsertion of Na+ in different MXene materials have been elaborated at the atomic level. The calculated results show that the surface terminated MXenes have a very low barrier for the diffusion of Na+ and Al3+, as shown in Figure 6. In addition, Na+ can also be electrochemically intercalate/deintercalate reversibly into MXene (Ti3C2Tx) lattice through solid solution reaction and phase transition.

It show that the Na+ can diffuse inside of Ti3C2Tx without much stretch. Therefore, as the anode material for the SIB, Ti3C2Tx displays excellent rate performance and stability in long cycle.[110,113,114] For many MXenes, the experimental and computational results are in good agreement in term of high rate performance.[115] At a high current rate of 10 C, the capacity of MXene electrodes decays to 50 mAh g−1.[50] Interestingly, when the thickness of 2D Ti3C2Tx flake decreased to the atomic level, its capacity increased by 1278 mAh g−1. Furthermore, computational studies show that both the open circuit potential and the low energy barrier can coexist in the single layer of TiC (Figure 7). As we all know, the metal properties of TiC remain unchanged after the formation of Na+ double layer, which guarantees excellent electronic conductivity and long cycle life.[116]

These exciting features of single-layer TiC recommend it for the rich metal character MXene, an encouraging SIB
In addition, the hetero and hierarchical structures of MXene composites also play an important role in improving the storage capacity of Na⁺. Furthermore, the electrochemical properties of MXene in organic electrolytes is limited. The main reason for limiting electrochemical performance is that in organic electrolytes, the size of loaded ions is larger than that in aqueous electrolytes, and the conductivity of the electrolytes is lower than that in aqueous electrolytes. Although there is a potential energy storage space between MXene layers, the interlayer spaces between MXene layers are small and its energy storage performance is limited. By introducing pillars between MXene layers and increasing the distance between MXene layers, more storage and transport space can be provided for ion loading, and electrolyte wetting can be promoted. For a detailed explanation of layer spacing or structural changes, Bak et al. reported the mechanism of Na⁺ intercalation and structural change in the MXene electrode in 2017, as shown in Figure 8. In this work, the charge storage mechanism of V₂CTₓ is studied. The 1st and 2nd charge-discharge profile measured in the potential window of 3.0–0.1 V at a current density of 10 mA g⁻¹, as shown in Figure 8b. The discharge capacity of the initial cycle is 220 mAh g⁻¹, which is irreversible with low Columbic efficiency as 53%, while the specific capacity of 2nd discharge cycle is 125 mAh g⁻¹. As mentioned previous, the irreversible capacity loss is caused by the formation of SEI film and the decomposition of electrolyte. Even though, in the following cycles, the reversible capacity is 90 mAh g⁻¹ at 10 mA g⁻¹. The rate capability is excellent when measured at different current densities up to 1 A g⁻¹. Interestingly, when the current density returns to 10 mA g⁻¹, V₂CTₓ shows a capacity of 83 mAh g⁻¹ (Figure 8c). In addition, at the current density of 20 mA g⁻¹, V₂CTₓ showed cycle stability with a capacity of 78 mAh g⁻¹ after 100 cycles. The excellent cycling stability and excellent rate capability indicate that V₂CTₓ is a promising energy storage systems electrode. In order to study the reasons of cycling stability and excellent rate capability, in-situ XRD was carried out, as shown in Figure 8d. During the first discharge/sodiation process, the peak of the XRD peak shifted from 9.3° to 8.1°. This shift to a low angle indicates that the lattice distance increases when the sodium-ion is inserted into the MXene electrode. Interestingly, when battery is charged/desodiated to 3 V, the lattice does not contract back to its original state, as shown in Figure 8a. This means that the Na⁺ does not completely separate from the V₂CTₓ layer, and some Na⁺ creates a pillar effect. Figure 8d clearly shows that during the 6th cycle of charge-discharge the XRD peak A and B both are present at 0.1 V and fully charged state at 3 V.
but the intensity of peaks slightly decreased, it means there are two types of lattice spaces are present and suggesting the Na\(^+\) entrap in the layers.

Hence, the entrapment of Na\(^+\) or pillared effect which keeps the lattice spacing constant in the subsequent sodiation and desodiation process, is the reason of excellent electrochemical

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**Figure 7.** Optimized single layer structure of TiC\(_3\) for ultrafast sodium storage. a) Map of electron localization function, b) top view of TiC\(_3\) symmetry, and c) diffusion energy barrier as low as 0.18 eV and diffusion length as 5.51 Å. Reproduced with permission.[136] Copyright 2018. American Chemical Society.

**Figure 8.** a) Schematic diagram of the interlayer change during the insertion/deinsertion of V\(_2\)CT\(_x\), b) charge/discharge curves of V\(_2\)CT, between 0.1 and 3.0 V potential window at a current density of 10 mA g\(^{-1}\), c) rate capability of V\(_2\)CT, d) ex situ XRD patterns of the 1st and 6th charge/discharge cycles. Reproduced with permission.[139] Copyright 2017. Wiley-VCH.
performance and reversible reaction. On the other hand, Kajiyama et al.\cite{138} reported the storage mechanism of Na$^+$ in Ti$_3$C$_2$Tx through theoretical and experimental studies. Theoretical study shows that with the desolvation of Na$^+$, the interlayer spacing of HO- terminated Ti$_3$C$_2$Tx increases significantly than that of other terminated Ti$_3$C$_2$Tx (Figure 9a–d). In this study, the Ti$_3$C$_2$Tx displays 270 mAh g$^{-1}$ capacity in the initial cycle and 145 mAh g$^{-1}$ in the second cycle. The SEI film formed by the decomposition of electrolyte avoids the further decomposition of electrolyte, stabilizes the subsequent cycling and alleviates the capacity fading, as shown in Figure 9e. The mechanism of cycling stability and structural change was predicted by ex situ XRD and nuclear magnetic resonance (NMR) (Figure 9g).

In the first sodiation process, the XRD peak moves to a lower angle (9.7 to 12.5 Å), which is due to the expansion of lattice space after Na$^+$ intercalation. However, in the first charge/desodiation process, the lattice contraction is very small, which can be clearly seen from the XRD pattern. Interestingly, in the following cycles, the lattice space of Ti$_3$C$_2$Tx remains unchanged, which indicates that Na$^+$ traps in the lattice of Ti$_3$C$_2$Tx, thus generating the pillared effect, which has been confirmed by the NMR study (Figure 9f) and HRTEM images shown in Figure 9g (right panel). Ex situ NMR measurements show that there are three different types Na ions in the sodiated and desodiated lattice of Ti$_3$C$_2$Tx. Finally, both Bak and Kajiyama confirmed the presence of pillared Na$^+$, which is conducive for the subsequent stable cycle after the initial cycle.

Therefore, under the same trend of opening the interlayer spacing for cycle stability, Luo et al.\cite{140} reported the pretreatment of Ti$_3$C$_2$ MXene by cetyltrimethylammonium bromide (CTAB) to open the interlayers of MXene forcefully, This provides an opportunity for the successful pillaring of S atom, which is covalently bonded on the surface of Ti$_3$C$_2$ (CT-S@Ti$_3$C$_2$) by heat diffusion method (Figure 10a). The results show that after CTAB treatment, elemental S easily embedded in the interlayer of Ti$_3$C$_2$. During the heat treatment, elemental S embedded in the interlayer and combined with Ti atom on the interface of Ti$_3$C$_2$ MXene to obtain S atom pillared Ti$_3$C$_2$ (Figure 10a). Furthermore, from the microstructure analysis, electrochemical performance evaluation, dynamic analysis, and DFT calculation, it is confirmed that the S atom pillared (CT-S@Ti$_3$C$_2$-450) is much effective as compared with other pillared Ti$_3$C$_2$. In the sodium storage process, the interactions between the interlayer Ti–S bond and Na$^+$ effectively open the interlayer of Ti$_3$C$_2$ MXene, as shown in Figure 10a,d,e. The interlayer spacing of S atom pillared CT-Ti$_3$C$_2$ is (1.37 nm) more significant than that simple CT-Ti$_3$C$_2$ and S@Ti$_3$C$_2$, which proves that the sulfur atom embedded CT-Ti$_3$C$_2$ is much efficient for the storage of Na$^+$. The results show that CT-S@Ti$_3$C$_2$-450 MXene has a larger space for Na$^+$ storage, and shows ultrafast Na$^+$ storage kinetics and a significantly increased energy storage site as clearly shown in Figure 10f–h. At the current density of 15 A g$^{-1}$, the capacity is still 120 mAh g$^{-1}$. A sodium-ion capacitor (CT-S@Ti$_3$C$_2$-450//AC SiC) was assembled by using CT-S@Ti$_3$C$_2$-450 as a negative electrode material and

Figure 9. Optimized geometries of Na$^+$ intercalated Ti$_3$C$_2$Tx, representing different interlayer spaces with different surface terminals groups, a) Ti$_3$C$_2$Tx, b) HO-/F-, c) O-/F-, d) F-/F terminated. The geometries from (a–d) indicates that MXene terminated with HO- and F- has a large interlayer spacing; e) Cyclic performance of Ti$_3$C$_2$Tx, showing good stability after 5 initial cycles; f) Deconvulated NMR spectra; g) Ex situ XRD patterns of the first two charge/discharge cycles and corresponding TEM images. Reproduced with permission.\cite{138} Copyright 2016. American Chemical Society.
commercial AC as positive electrode material. CT-S@Ti$_3$C$_2$-450 supercapacitor exhibits a high energy density of 263.2 Wh kg$^{-1}$ (based on the mass) at a power density of 8240 W kg$^{-1}$.

After 10,000 cycles, when the current density is 2 A g$^{-1}$, the capacity retention rate is 73.3%. Besides, the strategy of increasing interlayer space through covalent bonding of functional groups, which improves the electrochemical performances, MXene composites can also improve electrochemical performance remarkably.

Recently, Zhao et al.\textsuperscript{[141]} assembled PDDA-BP/Ti$_3$C$_2$ stack heterojunction by electrostatic adsorption (PDDA is Poly(diallyldimethylammonium Chloride) Figure 11a. Due to the face to face between the two components, almost all active sites are located on the surface, which leads to the dominant pseudocapacitance behavior. The parallel 2D interlayer spacing provides an effective channel for charge transfer and ion diffusion and accelerates the electrochemical kinetics process. DFT calculation shows that the strong interaction between BP and Ti$_3$C$_2$ can effectively reduce the binding energy between Na and BP. More importantly, the BP nanoparticle in PDDA-BP/Ti$_3$C$_2$ heterojunction material can be converted into monodisperse BP nanoparticles, which are distributed between Ti$_3$C$_2$ nanosheets through chemical action, to buffer volume expansion and prevent BP aggregation, and as a stronger synergistic adsorption site, accelerate the intercalation process of sodium. At the current density of 0.1 A g$^{-1}$, it shows 1112 mAh g$^{-1}$ super high reversible capacity after 500 cycles, even when the current density is 2.0 A g$^{-1}$, it could still maintain 464 mAh g$^{-1}$ reversible capacity, with excellent cycle stability and rate performance. More importantly, after 2000 cycles at 1.0 A g$^{-1}$, the reversible capacity of $\approx$658 mAh g$^{-1}$ was obtained (Figure 11c,d). The average capacity decay is 0.05% per cycle, showing the stability of the super long cycle. In addition, the electrochemical performance of PDDA-BP/Ti$_3$C$_2$ heterojunction electrode is better than that of BP/Ti$_3$C$_2$ electrode, which improves the utilization of BP material. In addition, PDDA-BP/Ti$_3$C$_2$ shows that MXene composite with large interlayer space electrode has obvious advantages.

From the above discussed literature and research progress, it can be seen clearly that the electrochemical performance of SIBs is controlled by several factors, such as type of MXene, interlayer spacing, termination, and electrode structure. Contrasted with Li-ion, Na-ion has bigger size. Therefore, the diffusion Na$^+$ is slower than that of Li$^+$. In order to achieve the
cycle stability and energy density of SIBs, MXene materials must have a large interlayer spacing or a pillared structure generated by composite strategy. Because, from the above work, we can see that the electrochemical performance becomes excellent when the interlayer spacing increases due to the pillaring effect (after the first cycle) or composite formation. The design of high performance MXene based electrode materials for SIBs is a key task in the future.

4.2. Potassium-Ion Storage

In recent years, compared with Li, Na, Mg, and Al, PIBs have many advantages, such rich raw materials, low price and low standard potential ($-2.92$ V vs SHE), which have attracted much attention. Theoretically, PIBs can provide higher discharge potential and energy density, which is an ideal alternative to LIBs. In addition, the successful application of commercial graphite anode in PIBs lays a foundation for the commercialization of PIBs in the future. However, the large size of $K^+$ also brings severe challenges to the development of potassium storage electrode materials. Due to the large size of $K^+$ ($d = 1.38$ Å), the insertion/deinsertion behavior in the active material seriously destroys the internal structure of the material, resulting in short cycle life and poor rate performance. Therefore, the development of electrode materials with high cycle stability and large volume strain tolerance is the key to the successful application of PIBs. Among all kinds of anode materials, carbon-based materials have attracted considerable interest of researchers due to their abundance, low potential and low cost and have broad application prospects in PIBs. However, compared with Li$^+$, the kinetics of $K^+$ in active materials is slower, which leads to lower initial Coulombic efficiency and poor rate performance in practical application. From this point of view, increasing the interlayer spacing of the heterostructured composite can reduce the $K^+$ insertion barrier and improve the electrochemical performance, which is expected to solve the above problems. In view of this, MXene has the
good advantage of high specific surface area, hydrophilicity, and adjustable interlayer spacing. It is an excellent ionic and electronic conductor, which make it different from other 2D layered materials. Although MXene materials have excellent cycle stability and rate performance for PIBs, its theoretical specific capacity is only 191.8 mAh g\(^{-1}\). At present, Ti\(_3\)C\(_2\) is prone to irreversible agglomeration and stacking, resulting in its actual specific capacity much lower than the theoretical value. In order to solve the above problems, optimize the interlayer structure, build a 2D hierarchical heterostructure, reduce the self-stacking effect, construct additional potassium storage sites and ensure that the K\(^+\) fast transmission channel can effectively improve its reversible capacity and rate performance.

Recently, Zhao et al.\textsuperscript{[142]} reported the heterostructure PDDA-NPCN/Ti\(_3\)C\(_2\), on the molecular scale. It is prepared in a face-to-face manner by electrostatic interaction between several layers of Ti\(_3\)C\(_2\) MXene and N-rich porous carbon nanochips (NPCN) (Figure 12a). PDDA-NPCN/Ti\(_3\)C\(_2\) heterojunction has a layered structure and large specific surface area, which can ensure the close contact between Ti\(_3\)C\(_2\) and NPCNS, and effectively utilize two components and more accessible active sites. After 300 cycles at 0.1 A g\(^{-1}\), the reversible capacity of the heterojunction material is 358 mAh g\(^{-1}\) (Figure 12c) and after 2000 cycles at 1.0 A g\(^{-1}\), it displays a reversible capacity of 252 mAh g\(^{-1}\) with a decay rate of only 0.03% per cycle (Figure 12d). As shown in Figure 12b, in the first depotassium process, the NPCNS nanoflakes in PDDA-NPCN/Ti\(_3\)C\(_2\) heterojunction material are converted into KC\(_{36}\), KC\(_{24}\), and KC\(_{8}\) nanoflakes, and then converted into NPCN nanoflakes, which are evenly dispersed and limited between Ti\(_3\)C\(_2\) flakes to buffer the volume expansion and prevent the aggregation of NPCN. In order to realize the excellent cycle stability and rate performance of hybrid (PDDA-NPCN/Ti\(_3\)C\(_2\)) anode, the ex situ XRD analysis of the electrode after the first charge/charge process was studied to explore the structure advancement. Figure 12b shows that, the XRD pattern is clear enough to reflect the diffraction characteristics of the hybrid anode. After K\(^+\) insertion, the peak height of NPCNS gradually decreased and shifted to a lower angle, indicating that K\(^+\) insertion increased the layer spacing of NPCNS. It is worth noting that the diffraction peak of NPCNS did not disappear until the potential reached 0.30 V, and a new peak appeared at 22.0° and 29.41°, which can be attributed to KC\(_{36}\). In addition, after further discharge, KC\(_{36}\) is further converted into KC\(_{24}\), which is well consistent with the new diffraction XRD peak at 20.2° and 30.61°. At the end of complete potas- siation, a new characteristic diffraction peak appears at 16.2° and 33.51°, attributed to the pure phase of KC\(_{8}\). After inser- tion of K\(^+\), the interlayer spacing of NPCNS increased from 4.08 to 5.37 Å, which is beneficial to buffer the volume expansion of NPCNS, reaching 31.6%. The final product (KC\(_{8}\)) after complete discharge process makes the potential platform much higher than that of potassium metal, reducing the risk of dendrite formation. Meanwhile, the diffraction peak (001) of Ti\(_3\)C\(_2\) moved to a lower angle, representing that the interlayer spacing expanded from 19.2 to 24.6 Å, which is consistent K\(^+\) intercalation into PDDA-NPCN/Ti\(_3\)C\(_2\) anode. The heterojunction hybrid material provides a larger interlayer spacing and a unique 3D interconnection conductive network to accelerate the ion/electron transfer rate. At the same time, this robust heterojunction material has high chemical stability because of
its good tolerance to the volume change caused by the phase change in the process of rapid charging and discharging. Furthermore, DFT calculation shows that PDDA-NPCN/Ti$_3$C$_2$ heterojunction can effectively reduce K$^+$ adsorption energy and accelerate reaction kinetics. This material has excellent potassium storage performance, which is due to the stacking structure of heterojunction material to ensure close contact between Ti$_3$C$_2$ and NPCN, thus effectively using the two components. The PDDA-NPCN/Ti$_3$C$_2$ heterostructured material has unique composition and high interlayer spacing, which provides significant capacity, excellent cycle performance, excellent rate performance and exceptional good rate capability for PIBs. These results proposed a new strategy to prepare high performance MXene based PIB anode. It paves the way for the application of self-assembled heterojunction materials in the energy storage system.

Furthermore, emphasize the importance of MXene heterostructure and composites. Huang et al.\textsuperscript{[144]} reported in 2019 that carbon-coated MoSe$_2$/MXene was used for K$^+$ ion storage. The 2D ultrathin nanosheets of MoSe$_2$ were decorated on the surface of MXene flakes by self-linking oxygen atom at the terminal of the surface to prepare a 3D hierarchical heterostructure (Figure 13a). These ultrathin nanosheets buffer the volume strain by increasing interlayer spacing. Moreover, the carbon coating on the MoSe$_2$/MXene strengthen the structure and conductivity of MXene. In addition, there is a strong chemical interaction between MXene flakes and 2D sheets of MoSe$_2$, which is conducive to the durability of the structure. The heterostructure MoSe$_2$/MXene@C has excellent electrochemical performance with ultra-fast K$^+$ insertion and deinsertion. At a current density of 200 mA g$^{-1}$, it displays reversible capacity of 355 mAh g$^{-1}$ after 100 cycles. Furthermore, as shown in Figure 13c,d, it shows extraordinary cycle stability and rate capability. At a high current density of 10 A g$^{-1}$, it shows 183 mAh g$^{-1}$ reversible capacity. The excellent performance of MoSe$_2$/MXene@C heterostructures, such as excellent rate performance and outstanding cycle stability, also supports the above conclusion. In other words, MXene heterostructure hybrid composite has a large layer spacing, can withstand the volume expansion of large size K$^+$ insertion and deinsertion, and has excellent electrochemical performance.

Furthermore, in order to enhance K$^+$ kinetics, Ming et al.\textsuperscript{[145]} designed a general method for preparing porous MXene electrode materials, which can significantly enhance K$^+$ storage performance (Figure 14a). The authors chose V$_2$C MXene as a typical representative and found that the potassium storage capacity of V$_2$C MXene material was significantly improved after simple alkali/acid treatment. In this method, MXene was prepared by fluoride salt etching and KOH treatment. Due to the intercalation of K$^+$ in KOH solution, the product has a large layer spacing. It is found that the final product K-V$_2$C MXene not only shows a specific capacity of 195 mAh g$^{-1}$, but also has good rate performance (Figure 14i). As a contrast, the original V$_2$C MXene material can only give specific capacity of 98 mAh g$^{-1}$. Furthermore, K-V$_2$C was used as the negative electrode and Prussian blue analogue as the positive electrode to prepare the full cell. All full cell electrochemical test shows that the average working voltage of K-V$_2$C//PB battery is as high as 3.3 V and it has excellent rate performance. Moreover, it achieves the energy density of 145 W h kg$^{-1}$ at a power density of 112.6 W kg$^{-1}$. In

![Figure 13.](image)

Figure 13. a) Schematic illustration of the synthesis of MoSe$_2$/MXene@C, b) Cycling performance of MoSe$_2$/MXene@C, c) Cycling performance of MoSe$_2$/MXene@C at three different current densities, d) Rate capabilities of MoSe$_2$/MXene@C up to high rate as 15 A g$^{-1}$. Reproduced with permission.\textsuperscript{[146]} Copyright 2019, American Chemical Society.
addition, the mechanism involved in the electrochemical reaction of K-V₂C MXene electrode was studied in detail to understand the reason of its excellent electrochemical performance. The phase structure changes in the repeated charge/discharge cycle were observed by in situ XRD and NMR (Figure 14e–h). The (002) diffraction peaks present noticeable lattice changes upon different charge and discharge states (Figure 14e,f). In the initial process of potassiation, the peak of (002) XRD moved a little to a lower angle and widened. Unexpectedly, when the battery discharged to 1.0 V, a new and small XRD peak can be observed at a lower angle. This new peak can still be observed at full charging of 3.0 V. It should be noted that the (002) peak is widened and will not return to its original state even under the cut off potential. In order to understand this phenomenon, in situ XRD was carried out in the fifth cycle of the K-V₂C electrode (Figure 4f). Curiously, unlike the initial cycle, the (002) peak displays a reversible shift. Furthermore, Figure 14g shows the instinctive comparison of the first and fifth cycles. During the discharge process, the (002) peak widened and shifts slightly to a low angle, then shrinks during charging. Similar to the previous report on the storage of Na⁺ in MXene,[138,146,147] it is assumed that the co-insertion of solvent and K⁺ produces new and small peaks at a lower angle. In the fully charged state, a prominently broader peak can be observed, indicating that a certain quantity of solvated K⁺ is inserted between MXene interlayers. To demonstrate this assumption, the cycled electrodes in the first and fifth full discharge and charge cycles were dried in a vacuum at 200 °C to remove the solvent. Figure 14g shows the XRD pattern of the dried product. It is exciting that there is no additional small peak at a lower angle, and the diffraction patterns of the four dried samples are clearer than those of the nondried samples. This outcome approves the assumption of solvent insertion. It is worth mentioning that the peak (002) of the dried sample still appears at a lower angle, which corresponds to the interlayer spacing between MXene layers due to the K⁺ trap, and the layer spacing increases from 9.38 to 9.63 Å. The storage behavior of K⁺ also studied by ⁳⁹K NMR. As shown in Figure 14h, the spectrum displays a signal at around −50 to −30 ppm, which is deconvoluted into high-resolution peaks. A deconvoluted peak at −38.5 ppm (Peak A) corresponds to the solvated K⁺ in the residual electrolyte.[148,149] Because the K⁺ in the electrolyte is actively shielded by the electrons provided by solvents and counter-ions, the peak B appears at a negative frequency around −39.3 ppm.[149] While, a wider linewidth indicates an inferior movement of K⁺. This kind of K⁺ can be allocated in the edge and surface of K-V₂C nanochips and SEI film. On the other hand, the negative shift peak C is significant and the linewidth wider, which indicates that the shielding effect is greater and the mobility is lowest. This can be justified by the robust interaction between the K⁺ and adjacent layers of K-V₂C. In the sense of the above discussion, the NMR spectrum for the fifth cycle (full discharge/charge) shows reversible solvated K⁺ insertion/deinsertion because, the peak C is stronger in discharge state than the charge state. In the first few cycles, the electrolyte is decomposed to form SEI, and in the process of deinertion, a definite amount of solvated K⁺ is pillared in the MXene layers at the same time, resulting in irreversible expansion of the layer. This pillared structure enables K-V₂C MXene to have excellent rate capability and long-term cycle stability, as shown in Figure 14i–k. This shows that K-V₂C MXene or other porous MXene materials prepared by this method are very promising electrode materials for K⁺ storage.

Like the Na⁺ storage in SIBs, the K⁺ storage properties in PIBs are also controlled by the same factors, among which the

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Figure 14. a) Schematic illustration of synthesis of K-V₂C, FESEM images of b) V₂AlC, c) V₂C, and d) K-V₂C, e–g) ex situ XRD patterns, h) NMR spectra of the 5th charge and discharge process; i) Rate performance of V₂C and K-V₂C, j) charge/discharge profiles of K-V₂C at different current densities; k) Cycling performance of full capacitor devices, inset is the charge-discharge profiles of anode and cathode electrodes. Reproduced with permission.[145] Copyright 2019, Elsevier.
Most important are the expanded interlayer spacing and electrode structure. K⁺ has a larger size than Na⁺. Therefore, K⁺ diffusion is slower than Na⁺. In order to achieve high power and high energy density, MXene materials must occupy a higher inevitability in PIBs than those of SIBs and LIBs, and have higher reaction activity and smaller diffusion path. The results show that the heterostructure hybrid composite and large interlayer spacing are of the great significance to the development of high performance PIBs, because MXene large interlayer spacing of MXene can withstand the volume expansion of large size K⁺ insertion and deinsertion. The key task in the future is to design more suitable MXene electrode materials for PIBs.

### 4.3. Magnesium-Ion Storage

Magnesium has abundant resources in the world, and its price is only about 1/24 of that of metal lithium, which has created a good foundation for the development of MIBs. MIBs are not suffer from dendrite growth as LIBs. In order to avoid the safety problems caused by dendrite short circuit, it is necessary to develop MIBs to make it more secure. In the sense of energy safety problems caused by dendrite short circuit, it is necessary to explore appropriate experimental methods to enable the stable performance of MXene. Previous studies have shown that divalent Mg ions cannot be reversibly embedded in Ti₃C₂Tx, resulting in almost no storage capacity in Ti₃C₂Tx MXene.

Recently, Xu et al.[153] reported Ti₃C₂Tx MXene as an efficient cathode material for MIBs. In this work, they used the CTAB method of pre-embedded cationic (CTA⁺) surfactant cetyltrimethylammonium bromide to change the electronic characteristics of MXene, so that Ti₃C₂Tx MXene showed high storage capacity of magnesium ions. The results show that the surfactant can increase the interlayer spacing of Ti₃C₂Tx MXene, but only the cationic surfactant can promote the Mg²⁺ storage of MXene. XPS and DFT found that the embedded CTA⁺ cations reduce the diffusion barrier of Mg²⁺ on the surface of MXene (Figure 15b), thus significantly improving the reversible insertion/deinsertion performance of Mg²⁺ between MXene layers. The electrochemical performances show that the magnesium battery with MXene as the positive electrode exhibits high volume capacity (300 mAh cm⁻³ at the current density of 50 mA g⁻¹), excellent rate performance, excellent rate capabilities and cycling stability (Figure 15a,c,d). This study provides a new idea for the application of MXene in the field of electrochemical energy storage, and also provides a new choice for the selection of positive materials for MIBs. In order to sum up the application, we think that MXene with pre-expanded interlayer spacing shows excellent kinetic performance, in the diffusion process of strong electrostatic Mg²⁺, and can increase the interlayer spacing by pre-insertion of organic cations (e.g., CTA⁺) or Mg ions. In addition, MXenes with neutral surface can effectively reduce the strong electrostatic interaction between Mg²⁺ and the surface terminals, thus improving the diffusion kinetics of MXene. Moreover, Table 2 represents the comparison of different MXene materials for NLIBs.

### 4.4. Aluminum-Ion Storage

Compared with commercial LIBs, rechargeable AIBs are safer, cheaper, and have higher energy density, which are suitable for large-scale power grid and electric vehicles. However, due to the high charge density of Al³⁺ and the strong interaction between Al³⁺ and the host lattice (same as Mg-ion), only a few positive materials can meet the reversible de-intercalation of Al ions, and a large part of it is difficult to consider in terms of capacity and cycle life. In a recent study, VahidMohammadi et al.[167] studied the application of 2D layered carbide V₂CTx in the aluminum cathode (Figure 16b), and found that when the number of V₂CTx layers decreased, its electrochemical performance improved significantly.

Firstly, multilayer V₂CTx (ML-V₂CTx) is used as the positive electrode to explore its electrochemical performance, as shown in Figure 16c,f shows the cyclic voltammetry (CV) curve of ML-V₂CTx, revealing two broad cathodic and corresponding anodic peaks. At the current density of 10 mA g⁻¹, the initial irreversible discharge capacity was 335 mAh g⁻¹, which might be due to the decomposition of chloro-aluminate and other electrolyte components to form SEI film. After the first cycle, the discharge capacity decreased to 178 mAh g⁻¹, and after 20 cycles, the capacity decreased to 112 mAh g⁻¹, and the Coulombic efficiency also decreased from the beginning of 100% down to 90%. After that, the in situ XRD analysis (Figure 16d) shows that there is no phase change in the material during the charging and discharging process, and the reaction mechanism of ion embedding into the positive electrode is proposed. In addition, the reaction mechanism was further verified by HRTEM and XPS analysis. Then, the author delaminated the ML-V₂CTx by vigorous stirring in the solution of 1-methyl-2-pyrrolidinone and prepared a few layers of V₂CTx (FL-V₂CTx) as shown in systematic Figure 16a. It is found that the initial reversible discharge capacity is as high as 482 mAh g⁻¹ and the first discharge capacity is 162 mAh g⁻¹ (ML-V₂CTx is only 90 mAh g⁻¹) at the current density of 100 mA g⁻¹. At the high rate of 5000 mA g⁻¹,
the capacity of 50 mAh g$^{-1}$ is still retained; at the condition of charging current density of 1000 mA g$^{-1}$ and discharge current density of 100 mA g$^{-1}$, 76 mAh g$^{-1}$ is retained after 100 cycles, and the Coulombic efficiency is also kept at about 96.6%.

Considering the influence of the number of layers on the electrochemical performance, TBAOH-FL-V$_2$CTx was obtained by using intercalator TBAOH to further increase the layer spacing. When the current density of 100 mA g$^{-1}$, the initial discharge capacity of TBAOH-FL-V$_2$CTx is 922 mAh g$^{-1}$, and its electrochemical performance is 300 mAh g$^{-1}$ after first four cycles. When the current density is 200 mA g$^{-1}$, the electrode still faces the problem of capacity attenuation, but it is the smallest of all reported anodes of AIBs, as shown in Figure 16g. The charge discharge tests at different rates show that TBAOH-FL-V$_2$CTx has excellent rate performance (Figure 16h).

When the current density is 300 mA g$^{-1}$, the capacity is maintained at about 150 mAh g$^{-1}$, and the Coulombic efficiency is also maintained at 95%. Because of the irreversible unblocking of Al$^{3+}$ and the decomposition of electrolyte, the Coulombic efficiency is low. The TBAOH-FL-V$_2$CTx electrode has better electrochemical performance because of its higher and more uniform dispersion than FL-V$_2$CTx. V$_2$CTx MXene has been proved to be a high capacity embedded anode material for AIBs. Still, V$_2$CTx is the best-known anode material at present (Figure 16i). Furthermore, VahidMohammadi et al.[167] also reported the theoretical capacities of different MXenes against Al anode, as shown in Table 3. Interestingly, it is clear from the table that MXenes are suitable electrodes for AIBs.

We believe that the electrostatic interaction between Al$^{3+}$ ion and the potential termination surface of the host material (cathode) hinders the reversible (insertion/deinsertion) diffusion process of Al$^{3+}$ with high charge density, so it is necessary to explore the MXenes with the expanded interlayer spacing and the neutral surface. We hope that in the future, MXene will become the cutting-edge cathode material of AIBs. The further improvement of electrochemical performance needs more in-depth embedded mechanism research.

4.5. Supercapacitors

SCs are also called electrochemical capacitors. According to the energy storage mechanism, it can be divided into electric double-layer capacitor (EDLC), pseudocapacitor and hybrid capacitor. The electric double-layer capacitor uses the double electric layer formed by the interface between electrode and
electrolyte to store charge, which has the characteristics of high power density and low energy density. The pseudocapacitor uses the rapid redox reaction on the electrode surface to store electric energy, which has relatively high energy density, but short cycle life. \[168\] Hybrid supercapacitor is a new type of capacitor which combines the double electric layer capacitor and the pseudocapacitor. The energy density of hybrid supercapacitor is between the double electric layer capacitor and the pseudocapacitor, and the power density is equal to the electric double layer capacitor, so the power density and the energy density can be considered. At present, the hybrid supercapacitor and secondary batteries are the same. The energy density of supercapacitor is still relatively low. Therefore, it is necessary to evaluate the performance of MXene by volume-specific capacity and volume energy/power density, which is more suitable for actual application. The calculation formula of capacitor energy density is \( e = CV^2/2 \), in which \( C \) is the capacitance and \( V \) is the working voltage window. Therefore, there are two ways to improve the energy density of the MXene supercapacitor, one is to expand the working voltage window, and the other is to increase the capacitance.

Here, we discuss different approaches to improve the capacitance of SCs. As well, many research groups reported high capacitance using MXene electrode materials to increase the density of supercapacitors. In the past, however, it has been challenging to consider both energy density and power density of SCs. Therefore, MXene needs to be intercalated/modified, doped or composite with other materials. It can prevent MXene from stacking and improve the electrochemical performance of MXene. It is more reasonable to evaluate the performance of MXene by volume capacity and energy/power density, because in practical application, most supercapacitors are mainly limited by volume, and MXene has a high bulk density, which can effectively reduce the volume of supercapacitors and expand its application range. Therefore, it is necessary to evaluate the performance of MXene by volume-specific capacity and volume energy/power density, which is more suitable for actual application. The calculation formula of capacitor energy density is \( e = CV^2/2 \), in which \( C \) is the capacitance and \( V \) is the working voltage window. Therefore, there are two ways to improve the energy density of the MXene supercapacitor, one is to expand the working voltage window, and the other is to increase the capacitance.

Table 2. Comparison of electrochemical performance of NLIBs.

| Battery | MXene materials | 1st cycle capacity | 2nd cycle capacity | Last cycle capacity | Number of cycles | Current density | Ref. |
|---------|-----------------|-------------------|-------------------|-------------------|-----------------|----------------|------|
| SIBs    | V_{2}CT_{x}     | 220               | 110               | 80                | 8               | 10             | [139]|
| SIBs    | Ti_{3}C_{x}@Sb-0.5 | 175               | 160               | 150               | 8000           | 1000           | [154]|
| SIBs    | 2D-V_{2}CT_{x}  | 90                | –                 | –                 | –              | 550            | [132]|
| SIBs    | FeS_{2}@Ti_{3}C_{x} | 1500              | 800               | 550               | 7              | 100            | [155]|
| SIBs    | Ti_{3}C_{x}     | 250               | 140               | 90                | 100            | 20             | [138]|
| SIBs    | a-Ti_{3}C MNRs  | 95                | 85                | 50                | 500            | 200            | [156]|
| SIBs    | CT-S@Ti_{3}C_{450} | 600               | 560               | 492               | 100            | 100            | [140]|
| SIBs    | MoS_{2}-in-Ti_{3}C | 300               | 320               | 320               | 1600           | 1000           | [157]|
| SIBs    | CoNiO_{2}/Ti_{3}C_{x} | 460               | 280               | 200               | 150            | 100            | [158]|
| SIBs    | MoS_{2}/Ti_{3}C_{x} | 500               | 350               | 250               | 100            | 100            | [159]|
| SIBs    | f-Ti_{3}C_{x}-DMSO | 475               | 225               | 175               | 500            | 100            | [137]|
| SIBs    | Ti_{3}C_{x}/SnS_{2} (S:1) | 900               | 455               | 340               | 200            | 100            | [160]|
| SIBs    | 3D-Ti_{3}C_{x}  | 475               | 250               | 300               | 1000           | 2.5C           | [161]|
| SIBs    | Sb_{2}O_{3}/Ti_{3}C_{x} | 720               | 425               | 500               | 100            | 100            | [162]|
| PIBs    | Ti_{3}C_{x}     | 275               | 100               | 40                | 500            | 200            | [156]|
| MIBs    | Ti_{3}C_{x}/CNT | 80                | 85                | 75                | 500            | 1C             | [163]|
| SIBs    | NiCoP/MXene     | 700               | 450               | 300               | 2000           | 1000           | [164]|
| SIBs    | PDFA-BP/MXene   | 1750              | 900               | 700               | 2000           | 1000           | [141]|
| PIBs    | PDFA-NPCN/Ti_{3}C_{x} | 900               | 700               | 300               | 2000           | 1000           | [142]|
| MIBs    | Ti_{3}C_{x}     | 175               | 150               | 40                | 60             | 100            | [165]|
| MIBs    | Ti_{3}C_{x}/CTAB | 200               | 200               | 150               | 250            | 200            | [153]|
| SIBs    | M-NTO          | 375               | 220               | 150               | 150            | 200            | [50]  |
| PIBs    | MoSe_{2}/MXene@C | 550               | 310               | 350               | 300            | 1000           | [144]|
| MIBs    | Ti_{3}C_{x}@C   | 215               | 165               | 150               | 400            | 50             | [166]|
| AIBs    | FL-V_{2}CT_{x} | 180               | 175               | 100               | 100            | 200            | [167]|

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density. This is because, in the traditional electrode preparation method, the electrochemical performance of the 2D nanomaterial film highly depends on the thickness of the film. Increasing the thickness of the electrode film often leads to the decrease of ion transport performance. The increase in film thickness may lead to the accumulation of nanoparticles, so ion transport needs to go through a long and tortuous channel, just like the mountain road between mountains (Figure 17a). In order to improve the ion transport performance in thick films, the solutions proposed by people include: first, to enlarge the layer spacing and improve the ion transport capacity through intercalation, which is equivalent to widening the mountain road; second, to make defects on nanochips for ion transport, which is equivalent to adding some paths between mountain roads. All these methods are effective, but none of them can solve the problem fundamentally. Therefore, Xia et al. put forward a more systematic and effective third plan. Changes the assembly mode of 2D nanomaterials from parallel to electrode arrangement to vertical to electrode arrangement (Figure 17b), which is equivalent to first lifting the mountain, and then placing the mountain on both sides of the road. Then, the electrochemical properties of vertical array and parallel array MXene films compared. For the membrane obtained by suction filtration, when the membrane thickness increases from 6 to 35 µm, the pseudocapacitance decreases seriously. The thickness of MXLLC films increases from 40 to 200 µm, and the pseudocapacitance is almost the same. When the scanning rate is lower than 2000 mV s⁻¹ and the film thickness increases from 40 to 200 µm, the magnification performance of MXLLC film only slightly decreases (Figure 17j), which is significantly different from the results obtained by suction filtration. MXLLC electrode is very stable. When the current density is 20 A g⁻¹, the capacitance almost 100% after 20,000 constant current cycles. For 200 µm thick films, when the scanning rate is less than 2000 mV s⁻¹, the areal capacitance has exceeded the standard of supercapacitor electrode (0.6 F cm⁻²). Using the liquid crystal characteristics of 2D nanomaterials to control their orientation and arrangement in the dispersion, researchers developed a large-scale method to prepare vertically aligned nanofilms. Due to the improvement of ion transport properties, the thickness below 200 µm does not affect the charge storage capacity.

In addition, in order to enhance the capacitance and other electrochemical performances the arrangement of MXene supercapacitors, Lukatskaya et al. also reported a new strategy to improve the capacitance of MXene based supercapacitors. In this study, Ti₃C₂ MXene was intercalated with various ions to synthesized a “Ti₃C₂ paper” (p-Ti₃C₂), and then electrochemical performance was measured (Figure 18a–c). Because different ions are pre-intercalated between MXene layers, the interlayer space increases, resulting in high capacitance and electrochemical performance (Figure 18d–g).

A self-supporting electrode with a thickness of only 2–20 µm was obtained. In KOH electrolyte, the volume capacitance of
In addition to the pre-intercalated p-Ti$_3$C$_2$T$_x$ supercapacitor, the micro-supercapacitors (MSCs) also shows superior power density and longer cycle life.[100,101] MSC is an ideal independent power supply in the field of intelligent microelectronics such as nano robots, MEMS, distributed sensor networks, etc. However, it is rare that MSCs with high specific surface area have both high volume capacitance and high areal capacitance. Recently, Nicolosi’s group[171] reported an efficient and low-cost rapid printing production strategy, namely, expanded flexible MSCs (Figure 19). They use a new hydrophilic 2D MXene ink as active material with high conductivity, avoiding the need for additional additives or polymers.

As a result, a flexible full-MXene micro supercapacitors with a controlled structure can be manufactured, which can provide a flexible, efficient, and first-class power system for the new generation of microelectronic equipments. Compared with traditional manufacturing processes and direct ink printing technology, such as inkjet printing and extrusion printing, it brings digital and additional graphics, specialization, material waste reduction, scalability and rapid growth production, working capability and high capacitance in many bending cycles. The ink-JET MSC displays a capacitance of 512 F cm$^{-1}$, which is much higher than that of graphene MSC (≤100). Furthermore, at a power density of 11.4 µW cm$^{-2}$, the energy density of the extruded is 0.32 µW h cm$^{-2}$. Interestingly, both printed MSCs show high capacitance retention, with 97% for extrusion and 100% for inkjet printed.

On the other hand, in 2019, Zhang et al.[170] reported an efficient and low-cost expandable flexible MSCs rapid 3D printing stamping production strategy (Figure 20), using a new hydrophilic MXenes ink (Figure 20b) with high conductivity as active material, and MXene MSCs is shown in Figure 20c,d,j. Through SEM, the author examined the interdigitated Ti$_3$C$_2$T$_x$ MSC (I-Ti$_3$C$_2$T$_x$) on paper and found that the width of the interdigitated electrode was ≈450 µm and the gap is ≈550 µm (Figure 20e). There is no doubt that the uniformity of finger electrodes needs to be further improved, as shown in Figure 20f. Intricate patterns on the geometry of Yin-Yang and spiral Ti$_3$C$_2$T$_x$ MSCs, such as finger electrodes (labeled y-and S-Ti$_3$C$_2$T$_x$, respectively), can also be made in the same way (Figure 20d). In addition, MSCs on these papers are flexible and maintain an effective conductive network (charge resistance < 15%) during repeated bending/release. Interestingly, the devices remained stable after six months of exposure.

The interdigitated Ti$_3$C$_2$T$_x$ MSC fabricated in this study has a high areal capacitance. At 25 µA cm$^{-2}$, the areal capacitance is 61 mF cm$^{-2}$. When the current density increases by 32 times, the areal capacitance increases to 50 mF cm$^{-2}$. Not only that, Ti$_3$C$_2$T$_x$ MSC also have the characteristics of capacitor charge storage, excellent cycle life, high energy and power density (Figure 20h). The production of this high-performance Ti$_3$C$_2$T$_x$ MSCs can be enlarged by designing pads or cylindrical seals and then cold rolling process. In the process of cold pressing or rolling, dozens of MSCs with high areal capacitance (56.8 mV cm$^{-2}$ at 10 mV s$^{-1}$) were manufactured in a few seconds.

For a time, the electrochemical performances of MSCs fabricated by this stamping technique exhibited superior

### Table 3. Calculated theoretical capacities of MXene cathode materials against Al anode as reported by the ref. [167].

| Type of MXene | MAX Phase | MXene | Theoretical capacity [mAh g$^{-1}$] |
|--------------|-----------|-------|-----------------------------------|
| Carbides     | Ti$_3$AlC$_2$ | Ti$_3$C$_2$F$_2$ | 391 |
|              | Ti$_3$C$_2$O$_2$ | 402 |
|              | Ti$_3$C$_2$(OH)$_2$ | 398 |
| Cr$_2$AlC    | Cr$_2$CF$_3$ | 522 |
|              | Cr$_2$CO$_3$ | 543 |
|              | Cr$_2$(OH)$_3$ | 536 |
| Mo$_2$AC     | Mo$_2$CF$_3$ | 332 |
|              | Mo$_2$CO$_3$ | 340 |
|              | Mo$_2$(OH)$_3$ | 338 |
| Nb$_2$AlC    | Nb$_2$CF$_3$ | 340 |
|              | Nb$_2$CO$_3$ | 349 |
|              | Nb$_2$(OH)$_3$ | 346 |
| V$_2$AlC     | V$_2$CF$_3$ | 529 |
|              | V$_2$CO$_3$ | 551 |
|              | V$_2$(OH)$_3$ | 543 |
| Ti$_2$AlC    | Ti$_2$CF$_3$ | 531 |
|              | Ti$_2$CO$_3$ | 575 |
|              | Ti$_2$(OH)$_3$ | 567 |
| Sc$_2$AlC    | Sc$_2$CF$_3$ | 574 |
|              | Sc$_2$CO$_3$ | 600 |
|              | Sc$_2$(OH)$_3$ | 591 |
| Nitrides     | Cr$_2$AlN  | Cr$_2$F$_3$ | 515 |
|              | Cr$_2$NO$_3$ | 529 |
|              | Cr$_2$(OH)$_3$ | 536 |
| V$_2$AlN     | V$_2$F$_3$ | 522 |
|              | V$_2$NO$_3$ | 543 |
|              | V$_2$(OH)$_3$ | 536 |
| Ti$_2$AlN    | Ti$_2$F$_3$ | 544 |
|              | Ti$_2$NO$_3$ | 567 |
|              | Ti$_2$(OH)$_3$ | 559 |

$^a$MXenes are synthesized from Mo$_2$Ga$_2$C; $^b$MXenes are not synthesized yet, but their MAX phases are available.
characteristics than those previously reported MSCs (Figure 20i). By further optimizing the synthesis process of MXene, adjusting the composition of the MXene sheet, surface chemical treatment and stamping design, high areal capacitance and volumetric capacitance can be achieved. To sum up, this study proposed a new stamping strategy, which combines 3D printing technology with viscous MXene water-based ink to rapidly manufacture high-performance co-planar full MXene MSCs, providing a development opportunity with great application potential for the manufacture and application of printable energy storage devices. Therefore, a flexible full MXene MSC with controllable structure can be developed, to provide a flexible, efficient and first-class power system for the new generation of microelectronic equipment.

Finally, in addition to increasing the energy density and capacitance of the supercapacitor as mentioned above, the potential window is also very important to improve the electrochemical performance. Recently, Jiang et al. [172] reported a downup method to enhance the capacitance and a potential window for MXene based pseudocapacitors so for. In this study, for asymmetric pseudocapacitors, Ti3C2Tx ink grown on carbon fibers (CF) and RuO2 was also grown on CF hydrothermally, as shown in Figure 21a. The electrochemical performances were measured in 1 m H2SO4 electrolyte and PVA/H2SO4 gel electrolyte. The growth of Ti3C2Tx ink on CF is very smooth, as shown in Figure 21b,c. Interestingly, due to the high conductivity, wide potential window and proton induced capacitance of MXene and CF, the electrochemical performance is very significant. At 100 mV s−1, the specific capacitance of Ti3C2Tx/CF in 1 m H2SO4 is 350 F g−1, and at 20 A g−1, the capacitance retention rate after 20 000 cycles is 98%.

In contrast, the capacitance of asymmetric capacitor (RuO2//Ti3C2Tx full device) is 78 F g−1, and the capacitance retention rate is 86% after 20 000 cycles. So, MXene has excellent electrochemical performance as a negative electrode in asymmetric supercapacitors and asymmetric pseudocapacitors. It can be seen from the above literature that MXene electrode with new structure and MXene electrode and large interlayer spacing significantly improve the capacitance of MXene based supercapacitors. Furthermore, Table 5 shows the comparison of
5. Conclusions

Since the first report of MXene in 2011, it has become a hot and cutting-edge research direction in the field of 2D materials. In the aspect of material preparation, the existing MXene material preparation methods are mainly developed around the idea of etching MAX phase precursor, which belongs to the top-down method. There are many preparation methods to prepare MXene materials by choosing etchants. Different etching methods have different effects on the morphology of MXene materials. Although MXene materials can be prepared on a large scale by etching, more heteroatomic functional groups or structural defects are often introduced on the surface of MXene materials, thus affecting the conductivity of MXene. According to the preparation route of graphene and other 2D materials, the development of bottom-up methods such as CVD is the future direction of high-purity MXene preparation. In addition, there are more than 70 kinds of MAX phases, but only 20 MXenes have been successfully synthesized, and no more MXene materials have been synthesized. At present, most MXene materials reported by research institutes are Ti-based materials. With the change of metal element composition, MXene materials will show different properties. The exploration of different metals or bimetallic transition metals and multiple transition metals MXene materials is expected to open another window for the research of 2D materials. In the aspect of material structure design, whether 2D MXene nanowires or nanotubes can be prepared using the idea of graphene research and 2D MXene, and their properties can be studied, or MXene can be used as a template to prepare metal oxides and other derivatives with corresponding unique structure, which is also the work to be studied in the field of MXene materials.

MXene is a kind of 2D layered material with various components, hydrophilicity and conductivity, and adjustable surface properties.

Table 4. Lattice changes of Ti3C2Tx after ion intercalation and the original lattice space is 20.3 Å.

| Intercalant salt ions | Lattice value after intercalation of ions [Å] | Lattice value changed by ΔÅ |
|-----------------------|-----------------------------------------------|----------------------------|
| KOH                   | 25.4                                          | 5.1                        |
| NH4OH                 | 25.3                                          | 5.0                        |
| NaOH                  | 25.3                                          | 5.0                        |
| HCOONa                | 24.9                                          | 4.6                        |
| Na2CO3                | 24.9                                          | 4.6                        |
| CH3COONa              | 24.8                                          | 4.5                        |
| CH3COOK               | 24.6                                          | 4.3                        |
| CH3COOli              | 24.5                                          | 4.2                        |
| ZnSO4                 | 21.7                                          | 1.4                        |
| K2SO4                 | 21.4                                          | 1.1                        |
| MgSO4                 | 21.3                                          | 1.0                        |
| Na2SO4                | 21.0                                          | 0.7                        |
functional groups. It has obvious advantages in the field of Li, Na, K, Ca, Mg, and Al-ion batteries, supercapacitors and other energy storage fields, and relevant research is in full swing. It is clear from the above literature that MXene materials have excellent electrochemical performance in all non-lithium energy storage systems. However, there are still many problems to be solved. For example, the current experimental research is mainly focused on Ti$_3$C$_2$Tx, with a small amount of Ti$_2$CTx and V$_2$CTx involved. For this kind of MXenes, people have a good understanding of the structure and performance, while the preparation and research of other MXene are relatively few. When MXene is used as the electrode material of the secondary battery, its capacity still has a large space to improve. The stability and energy density of MXene based supercapacitor need to be further improved. The practical application of MXene supercapacitor in wearable electronic equipment needs to be developed. Its performance has exceeded graphene, which has been in development for nearly 17 years, especially in the field of energy storage.

6. Perspectives

At present, MXene has become a hot star material in the field of energy storage. In order to further promote the rapid development of MXene, the following aspects should be emphasized: 1) Find out the shortboard in the limited scale preparation of MAX and MXene, reduce the preparation cost, clarify the key factors affecting the preparation process from the source, and explore new and environment-friendly etching methods; 2) To explore the interaction mechanism between MXene nanotablets and various solvents, and to improve the life of MXene suspension in water and organic solvents, the strategies of adding antioxidants, film size, defect location and edge protection should be multi-channel; 3) To find out the influence of the surface chemistry of MXene on the properties; 4) Explore the packaging technology of devices; 5) Deepen the theoretical simulation calculation ability, and use the theoretical simulation to guide the selection of more potential MAX and MXene; 6) Development and application of MXene based solid secondary battery electrode; 7) Further, improve the volumetric capacity of MXene through reasonable structure design, and give full play to its advantages; 8) Flexible and transparent MXene film for the future Wearable Electronic equipment is of considerable significance; 9) MXene based hybrid supercapacitor takes into account both power density and energy density, which has high practical value and is worthy of great exploration, MXene based supercapacitors will play an important role in a harsh environment (such as the deep sea, high temperature and high-pressure environment).
Figure 20. a) Schematic illustration of 3D printing, stamping and ink formation, b) Optical photo of as-prepared viscous and thick MXene ink, c) Various stamps with required configuration, d) Different styles of MXene 3D printing MSCs, e) SEM image of the interdigitated Ti3C2Tx MSC (I-Ti3C2Tx) on paper and the width of the interdigitated electrode is ~415 µm and the gap is ~550 µm, f) High-resolution SEM image of printed ink on a paper substrate, g) CV curves, h) Long cycling performance with inset of GCD profiles at a current density of 200 µA cm⁻² of I-Ti3C2Tx, MSC, i) Comparison of the electrochemical properties of MSCs with different MXenes and I-Ti3C2Tx, j) MXene printing on different substrates. Reproduced with permission.[170] Copyright 2018, Wiley-VCH.

Figure 21. a) Schematic illustration of construction of ASC, b) FESEM image of CF coated Ti3C2Tx ink, c) FESEM image of CF with wrapped Ti3C2Tx coating, d) CV curves of Ti3C2Tx/CF at different scan rates, e) CV curves of the asymmetric device [Ti3C2Tx/CF/RuO2/CF] at different scan rates, f) CV curves of Ti3C2Tx/CF and RuO2/CF and asymmetric device at a scan rate of 50 mV s⁻¹, g) CV curves for single and double devices with inset of lighted LED by two devices. Reproduced with permission.[172] Copyright 2018, Wiley-VCH.
Table 5. A comprehensive data of previously reported MXene based supercapacitors.

| MXene materials          | Electrolyte | Capacitance     | No. of cycles | Cell Configuration       | Retention [%] | Year | Ref.   |
|--------------------------|-------------|-----------------|---------------|--------------------------|---------------|------|--------|
| Ti3C2Tx/MWCN             | 1 m Et4 NBf4 in ACS | 7 F g⁻¹ | 1000 at 20 mV s⁻¹ | 3-electrode system       | 100           | 2018 | [173] |
| Ti3C2Tx                  | 1 m H2SO4   | 54 F g⁻¹ | 1000 at 20 mV s⁻¹ | 3-electrode system       | 100           | 2018 | [173] |
| Ti3C2Tx/PANI             | 1 m Na2SO4  | 164 F g⁻¹ at 2 mV s⁻¹ | 3000 at 3 A g⁻¹ | 3-electrode system       | 96            | 2018 | [174] |
| Na2Ti3C2                 | 1 m KOH     | 160 F g⁻¹ at 5 mV s⁻¹ | 10 000 at 3 A g⁻¹ | 3-electrode system       | 91            | 2018 | [175] |
| Ti3C2Tx@MnO2             | 1 m Na2SO4  | 390 F g⁻¹ at 10 mV s⁻¹ | 6000 at 1 A g⁻¹ | 3-electrode system       | 93            | 2017 | [176] |
| Ti3C2Tx@CNT              | 6 m KOH     | 200 F g⁻¹ at 2 mV S⁻¹ | 10 000 at 1 A g⁻¹ | 3-electrode system and 2-electrode system | 78            | 2017 | [177] |
| Ti3C2Tx/wire             | PVA/KOH     | 4.64 F g⁻¹ at 0.1 mA s⁻¹ | 10 000 at 0.25 mA g⁻¹ | Parallel type            | 92            | 2017 | [178] |
| Ti3C2Tx@SCNT             | 1 m KOH     | 220 mF cm⁻² at 100 mV s⁻¹ | 10 000 at 10 A g⁻¹ | 3-electrode system       | 96            | 2017 | [179] |
| Ti3C2Tx@P3               | 1 m H2SO4   | 380 F g⁻¹ at 2 mV s⁻¹ | 10 000 at 100 mV s⁻¹ | 3-electrode system       | 98            | 2017 | [104] |
| Ti3C2Tx@EPD/PC film      | 1 m H2SO4   | 254 F g⁻¹ at 2 mV s⁻¹ | 10 000 at 10 A g⁻¹ | 3-electrode system       | 100           | 2017 | [180] |
| Ti3C2Tx@MXene/organic    | 1 m H2SO4   | 241 F g⁻¹ at 1 C  | 10 000 at 10 A g⁻¹ | 3-electrode system       | 100           | 2017 | [180] |
| Ti3C2Tx@MnOx             | 1 m Li2SO4  | 602 F cm⁻³ 200 mV s⁻¹ | 10 000 at 2 A g⁻¹ | 3-electrode system and 2-electrode system | 90           | 2017 | [182] |
| Ti3C2Tx@Cl               | 1 m H2SO4   | 180 F g⁻¹ at 2 mV s⁻¹ | –              | 3-electrode system        | –             | 2017 | [183] |
| Ti3C2Tx                  | PVA/H2SO4   | 600 F cm⁻³ 200 mV s⁻¹ | 8000 at 1 A g⁻¹ | 3-electrode system       | 90            | 2017 | [185] |
| Ti3C2Tx@CSC              | 1 m H2SO4   | 362 mF cm⁻² at 2 mV s⁻¹ | 1000 at 2 A cm⁻² | 3-electrode system       | 90            | 2017 | [185] |
| Ti3C2Tx@Ag-Nylon fibers  | PVA/H2SO4   | 50 mF cm⁻² at 2 mV s⁻¹ | 10 000 at 10 A g⁻¹ | Solid state              | 100           | 2017 | [186] |
| MXene@LDH                | 6 m KOH, PVA/KOH | 984 F g⁻¹ at 2 A g⁻¹ | 5000 at 30 A g⁻¹ | 3-electrode system, Solid state | 76            | 2017 | [187] |
| Ti3C2Tx/KOH              | 1 m H2SO4   | 500 F g⁻¹ at 1 mV s⁻¹ | 10 000 at 1 A g⁻¹ | 3-electrode system       | 99            | 2017 | [188] |
| Ti3C2CNTs                | 1 m Na2SO4  | 515 F g⁻¹ at 2 mV s⁻¹ | 5000 at 5 A g⁻¹ | 3-electrode system       | 95            | 2017 | [189] |
| Ti3C2Tx@PANI/TiO2        | 1 m KOH     | 188 F g⁻¹ at 10 mV s⁻¹ | 8000 at 1 A g⁻¹ | 3-electrode system       | 94            | 2017 | [190] |
| Ti3C2Tx@Hydrogel         | 1 m H2SO4   | 380 F g⁻¹ at 2 mV s⁻¹ | 10 000 at 10 A g⁻¹ | 3-electrode system       | 90            | 2017 | [191] |
| MoS2/C@PEDOT:PSS         | 1 m H2SO4   | 425 F g⁻¹ at 2 mV s⁻¹ | 10 000 at 5 A cm⁻² | 3-electrode system       | 90            | 2017 | [192] |
| MXene@GO                 | 1 m H2SO4   | 341 F cm⁻³ at 0.5 A cm⁻³ | 20 000 at 5 A cm⁻³ | 3-electrode system       | 100           | 2017 | [193] |
| TiC2                     | 6 m KOH     | 447 F g⁻¹ at 1 mV s⁻¹ | –              | 3-electrode system       | –             | 2017 | [194] |
| TiC2/N                   | 6 m KOH     | 156 F g⁻¹ at 5 mV s⁻¹ | 5000           | 3-electrode system       | V. little     | 2017 | [195] |
| MoS2/C paper             | 1 m H2SO4   | 1153 F cm⁻³ at 2 mV S⁻¹ | 10 000         | 3-electrode system       | 84            | 2017 | [196] |
| TiC2/N                   | 1 m H2SO4   | 82 F g⁻¹ at 1 mV S⁻¹ at -20°C | 10 000 at 50 mV s⁻¹ | 3-electrode system       | 92            | 2017 | [197] |
| TiC2/N                   | 6 m KOH     | 286 F g⁻¹ at 1 mV s⁻¹ | 2000 at 2 A g⁻¹ | 3-electrode system       | 79            | 2017 | [198] |
| TiO2/C@                  | 1 m KOH     | 60 mAh g⁻¹ at 1 A g⁻¹ | 5000 at 5 A g⁻¹ | 3-electrode system       | 70            | 2017 | [199] |
| Ti3C2Tx@MXene/NIO        | 1 m H2SO4   | 748 F g⁻¹ at 1 A g⁻¹ | 10 000 at 5 A g⁻¹ | 3-electrode system       | 98            | 2017 | [200] |
| Ti3C2/N                  | 1 m H2SO4, 6 m KOH | 442 F g⁻¹ at 1 A g⁻¹ | 5000 at 4 A g⁻¹ | GCD 2-electrode system, 3-electrode system | 92            | 2017 | [201] |
| TiC2@SnO2                | 6 m KOH     | 125 F g⁻¹ at 1 A g⁻¹ | 8000 at 3 A g⁻¹ | 3-electrode system       | 82            | 2017 | [202] |
| MSC TiC2Tx               | 1 m H2SO4, PVA/H2SO4 | 25 mF cm⁻³ at 20 mV s⁻¹ | 10 000 at 2 mA cm⁻² | 2-electrode system       | 92            | 2016 | [203] |
| MXene@EG                 | 1 m KOH     | 184 F cm⁻³ at 0.2 A cm⁻³ | 2500         | Solid state plane MSC    | 82            | 2016 | [204] |
| Ti3C2Tx@CNs              | Organic     | 80 F g⁻¹ at 2 mV s⁻¹ | 1000 at 10 A g⁻¹ | 3-electrode system       | 90            | 2016 | [205] |
| d-Ti3C2Tx                | 1 m H2SO4, PVA/H2SO4 | 49 F cm⁻³ at 0.63 A cm⁻³ | 1000 at 100 mV s⁻¹ | MSC 3-electrode system   | 87            | 2016 | [206] |

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Table 5. Continued.

| MXene materials | Electrolyte | Capacitance | No. of cycles | Cell Configuration | Retention [%] | Year | Ref. |
|-----------------|-------------|-------------|---------------|-------------------|---------------|------|------|
| Ti3C2@MnO2      | 6 M KOH     | 377 mF cm⁻² at 2 mV s⁻¹ | 5000 at 5 A g⁻¹ | 3-electrode system conventional | 95            | 2016 [207] |
| Ti3C2@ZnO       | 1 M KOH     | 120 F g⁻¹ at 2 mV S⁻¹ | 10 000 at 5 A g⁻¹ | 3-electrode cell | 86            | 2016 [208] |
| Ionogel Ti3C2T₃ | Liquid      | 70 F g⁻¹ at 20 mV S⁻¹ | 1000 at 1 A g⁻¹ | 2-electrode system | 80            | 2016 [209] |
| L-Ti3C2Tx       | PVA/H₂SO₄  | 356 F cm⁻¹ at 0.2 mA cm⁻² | 10 000 at 50 mV s⁻¹ | MSC               | 100           | 2016 [210] |
| Ti3C2(F)        | 3 M KOH     | 141 F cm⁻¹ at 2 A g⁻¹ | 1000 at 2 A g⁻¹ | Symmetrical SCs | 94            | 2016 [211] |
| Ti3C2@LDH       | 6 M KOH     | 1061 F g⁻¹ at 1 A g⁻¹ | 4000 at 4 A g⁻¹ | 3-electrode system | 70            | 2016 [212] |
| Ti3C2Tₓ@rGO     | 2 M KOH     | 154 F g⁻¹ at 2 A g⁻¹ | 6000 at 4 A g⁻¹ | 3-electrode cell | 85            | 2016 [213] |
| Ti3C2Tₓ@MoO₃    | 1 M KOH     | 150 F g⁻¹ at 2 mV s⁻¹ | 8000 at 1 A g⁻¹ | 3-electrode cell | 93            | 2016 [214] |
| 1-Ti3C2Tₓ/Ppy   | 0.5 M H₂SO₄, PVA/H₂SO₄ | 203 mF cm⁻² at 1 A cm⁻² | 20 000 at 1 mA cm⁻² | 3-electrode cell (solid state) | 100           | 2016 [103] |
| d-Ti3C2@CNTs    | 6 M KOH     | 393 F cm⁻¹ at 5 mV s⁻¹ | 10 000 at 10 mV s⁻¹ | 3-electrode system | 80            | 2015 [215] |
| Ti3C2@CNTs paper| 1 M MgSO₄   | 390 F cm⁻¹ at 2 mV s⁻¹ | 10 000 at 1 | 5 A g⁻¹ | –            | 2015 [216] |
| Mo₂TiC₂Tx       | 1 M H₂SO₄   | 420 F cm⁻¹ at 2 mV s⁻¹ | 10 000 at 1 | 1 A g⁻¹ | 100          | 2015 [217] |
| Ti3C2Tx         | H₂SO₄       | 499 F g⁻¹ at 2 mV S⁻¹ | 10 000 at 1 | 10 A g⁻¹ | 100          | 2015 [218] |
| Ti3C2            | 30% KOH     | 51 F g⁻¹ at 1 A g⁻¹ | 6000 | Coin type | 93            | 2015 [219] |
| Ti3C2Tₓ/PVA      | 6 M KOH     | 528 F cm⁻¹ at 2 mV s⁻¹ | 10 000 at 1 | 5 A g⁻¹ | –            | 2014 [92] |
| Ti3C2Tₓ-Clay     | 1 M H₂SO₄   | 246 F g⁻¹ at 2 mV s⁻¹ | 10 000 at 1 | 10 A g⁻¹ | 100          | 2014 [70] |
| Ti3C2Tₓ         | NaOAc/KOH/Mg SO₄ | 442 F cm⁻¹ at 2 mV s⁻¹ | 10 000 at 1 | 1 A g⁻¹ | 3-electrode system | 100           | 2013 [43] |
| Ti3C2@TiO₂       | 6 M KOH     | 143 F g⁻¹ at 5 mV s⁻¹ | 6000 | 3-electrode cell | 92            | 2016 [220] |
| Ti3C2@SnO₂       | 6 M KOH     | 125 F g⁻¹ at 1 A g⁻¹ | 8000 | 3-electrode cell | 82            | 2017 [202] |
| Ti3C2@ZnO        | 1 M KOH     | 120 F g⁻¹ at 2 mV s⁻¹ | 10 000 | 3-electrode cell | 85            | 2016 [208] |
| Ti3C2Tₓ/KOH-PVA  | 1 M KOH     | 530 F cm⁻¹ at 2 mV s⁻¹ | 10 000 | 3-electrode system | 83            | 2014 [92] |
| Ti3C2/Ppy        | PVA/H₂SO₄  | 530 F cm⁻¹ | 20 000 | Solid state | 100          | 2016 [221] |
| Ti3C2Tₓ/PFDS     | 1 M H₂SO₄   | 380 F g⁻¹ at 2 mV s⁻¹ | 10 000 | 3-electrode system | 98            | 2017 [104] |
| Ti3C2/PVDF       | 1 M KOH     | 117 F g⁻¹ at 2 mV s⁻¹ | 10 000 | 3-electrode cell | 98            | 2015 [222] |
| Ti3C2Tₓ/CNF      | 1 M NaClO₄  | 123 F g⁻¹ at 0.5 mV s⁻¹ | 500 | 3-electrode cell | 100          | 2016 [223] |
| Ti3C2/CNT        | Organic     | 85 F g⁻¹ at 2 mV s⁻¹ | 1000 | Swagelock cell | 90            | 2018 [205] |
| Ti3C2Tₓ/Graphene | 1 M H₂SO₄   | 33 F cm⁻¹ at 5 mV s⁻¹ | 2500 | 3-electrode cell | 82            | 2016 [185] |
| Ti3C2Tₓ/carbon   | 1 M H₂SO₄, PVA/H₂SO₄ | 530 mF cm⁻² | 1000 | 3-electrode cell | 96            | 2018 [185] |
| Ti3C2Tₓ/K+       | 6 M KOH     | 135 F g⁻¹ at 5 mV s⁻¹ | 5000 | 3-electrode cell | 95            | 2016 [207] |
| Ti3C2Tₓ-delaminated | 1 M KOH | 134 F g⁻¹ at 20 mV s⁻¹ | 5000 | 3-electrode system | 94            | 2017 [224] |
| Ti3C2Tₓ/KOH-PVDF | KOH         | 132 F g⁻¹ at 2 mV s⁻¹ | 10 000 | – | 100          | 2013 [43] |
| Ti3C2(F)        | 6 M KOH     | 118 F g⁻¹ at 5 mV s⁻¹ | 5000 | 3-electrode cell | 100           | 2016 [225] |
| Ti3C2Tₓ         | Organic     | 70 F g⁻¹ at 20 mV s⁻¹ | 1000 | 2-electrode Swagelock cell | 85            | 2016 [209] |
| Ti3C2Tₓ         | 3 M H₂SO₄   | 676 F cm⁻¹ at 20 mV s⁻¹ | 20 000 | 3-electrode system | 100          | 2017 [95] |
| Ti3C2Tₓ/DMSO     | 1 M H₂SO₄   | 520 F cm⁻¹ at 2 mV s⁻¹ | 10 000 | Swagelock cell | 100 | 2014 [226] |
| Ti3C2Tₓ/Ni-foam  | 1 M H₂SO₄   | 499 F g⁻¹ at 2 mV s⁻¹ | 10 000 | 3-electrode cell | 100 | 2015 [218] |
