Roles of Metal Ions in MXene Synthesis, Processing and Applications: A Perspective

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With a decade of effort, significant progress has been achieved in the synthesis, processing, and applications of MXenes. Metal ions play many crucial roles, such as in MXene delamination, structure regulation, surface modification, MXene composite construction, and even some unique applications. The different roles of metal ions are attributed to their many interactions with MXenes and the unique nature of MXenes, including their layered structure, surface chemistry, and the existence of multi-valent transition metals. Interactions with metal ions are crucial for the energy storage of MXene electrodes, especially in metallic batteries and supercapacitors with neutral electrolytes. This review aims to provide a good understanding of the interactions between metal ions and MXenes, including the classification and fundamental chemistry of their interactions, in order to achieve their more effective utilization and rational design. It also provides new perspectives on MXene evolution and exfoliation, which may suggest optimized synthesis strategies. In this respect, the different effects of metal ions on MXene synthesis and processing are clarified, and the corresponding mechanisms are elaborated. Research progress on the roles metal ions have in MXene applications is also introduced.

1. Introduction

Since graphite was delaminated to form graphene, there has been tremendous research interest on 2D materials in academia and industry, due to its remarkable physical and electronic properties. In recent decades, various other 2D materials besides graphene have been explored including transition metal dichalcogenides (TMDs), metal carbides/nitrides, layered double hydroxides (LDHs), boron nitride (h-BN), graphene-like single elements (e.g., black phosphorus), etc.[1–4] They typically have strong in-plane bonding and weak out-of-plane interactions, with very large exposed surface areas. Their properties can be effectively changed by altering their composition, interlayer structure, and surface chemistry, which gives them potential use in many fields, such as optoelectronics, catalysis, energy, sensors, and biomedicine.[5,6]

MXenes are a range of new 2D transition metal carbide/nitride materials with a functional structure, which were first discovered in 2011[7] and well defined in 2012.[8] This category of 2D materials shares the general formula $M_{n+1}X_nT_x$ ($n = 1–3$), where $M$ is a transition metal (e.g., Ti, V, Mo, Cr), and $X$ is carbon and/or nitrogen, with surface terminations indicated by $T$ (e.g., -O, -OH, -F, -Cl, -Br, -S, -NH, -Se, -Te). The presence of single or mixed terminations in MXenes is determined by their synthesis or processing.[9–11] In general, they are synthesized by selectively etching A layers from MAX phases, where A is a group of 13 or 14 elements (e.g., Al, Si, Ga), and M and X are the same as for the corresponding MXene. The first and the most studied

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MXene is Ti$_3$C$_2$T$_x$ (T = O, -OH, -F), which was first produced in 2011 with a hydrofluoric acid (HF) solution as the etchant.[17] The molten Lewis acid salt route enables other surface groups (i.e., -Cl, -Br, -I) to terminate the MXene surface.[12,13] Further termination substitution by -NH$_2$, -S, -Se, -Te, or complete removal can be achieved by substitution reactions. Modification of the surface chemistry enables fine-tuning of the band gap as well as other properties, such as electrical, optical, and optoelectronic.[14–18] For example, Liu et al. indicated that, compared with the bare surface, -O terminations tend to increase the work function of MXenes, while -OH terminations tend to cause a decrease. The tendency produced by -F terminations depends on the specific structure of the MXenes.[13] A superconducting transition behavior has been reported at low-temperatures for -S (or -Se, -NH) terminated Nb$_2$C, while no such a behavior occurs for Nb$_2$CO$_x$.[14] Till now, more than 30 MXenes with different compositions have been discovered experimentally, and over 100 different MXenes have been theoretically predicted. The M sites can also be filled by two or more transition metals to form solid solutions or ordered structures. This unique structure gives MXenes attractive electronic, optical, and magnetic properties. A transition metal carbide core gives MXenes metallic conductivity (20 000 S cm$^{-1}$ for Ti$_3$C$_2$T$_x$), and multi-valent transition metals ensure good redox activity. The layered structure surface terminations provide active sites, solution dispersion ability, and the ability to change properties. Through strategic design and controlled synthesis, MXenes have proven to be promising in various applications, such as supercapacitors, rechargeable metal-ion batteries, catalysis, electromagnetic interference (EMI) shielding, and water treatment.[19–21]

The layered structure, abundant surface terminations, and redox activity of MXenes allow them to be altered in a variety of ways, when coupled with different metal ions. Metal ions (e.g., Li$^+$, Na$^+$, K$^+$) are found to be spontaneously or electrochemically intercalated between MXene layers.[22] In the case of spontaneous intercalation, delamination of the MXene and expansion of the interlayer spacing can be achieved. Controlling the interlayer spacing is generally supposed to be an effective way of changing the band gap, Fermi level, conductivity, and other properties of 2D materials. Furthermore, the intercalated metal ions hardly change the lattice structure of MXenes and still maintain high ion mobility.[14,23,24] Electrochemical intercalation induces changes in the chemical potential and redox state of MXenes, which plays a significant role in the energy storage in metal ion batteries.[25,26] Interestingly, some metal ions behave differently and may induce a dramatic structural or lattice change of MXenes.[27] For example, divalent metal ions (e.g., Fe$^{2+}$, Mg$^{2+}$) can trigger crosslinking to form a 3D network, which is beneficial for ion diffusion.[28,29] Some metal ions with redox activities (e.g., Fe$^{3+}$, Cu$^{2+}$) may generate atomic defects, pores, or produce MXene degradation. Because of the redox activities of metal ions and MXenes, MXene sheets with anchored metal atoms or nanoparticles can be synthesized in a one-step method.[30,31] The evolution from MAX to MXene also involves metal ions, such as A$^{x+}$ oxidized from the A atoms in MAX by etchants, examples being Li$^+$ in the LiF/HCl route and Cu$^{2+}$ in the molten CuCl$_2$ route. Considering that the quality of MXene sheets highly depends on the preparation process (including the etching reaction and delamination), it is vital to figure out the role of metal ions in MXene synthesis and the interactions between them.

Based on the above, it is necessary to have insight into the interactions between metal ions and MXenes. Specifically, from the perspective of MXenes, abundant surface terminations coupled with different metal ions permits effective structure control, including the interlayer structure (including interlayer spacing, surface groups, and some surface doping) and 3D structure. The modification of targeted surface terminations can be achieved by chain effects produced by metal ions, such as -Cl terminations produced by etching the MAX precursors in molten MCl$_x$ salts, and -O terminations by treating MXenes in KOH solutions.[32–34] Furthermore, the transition metals in MXenes have many valence states, which provides many possible interactions with metal ions and can cause in-plane defects, such as atomic vacancies and pores. While, from the perspective of metal ions, their interactions with MXenes can induce ion adsorption, anchoring, or in-situ reduction, and can also form uniform active sites or nucleation sites for the production of MXene-based metal composites. In addition, metal ions play a role as charge carriers in rechargeable batteries, and their interactions with MXenes determine the electrochemical performance. With these direct or indirect interactions, MXenes have been used for electrode materials in supercapacitors and rechargeable batteries, as excellent supports for single-atom or hybrid catalysts, and key materials in water treatment. One of the primary targets is to develop an environmentally friendly and effective strategy for controlled MXene synthesis and the exploration of new MXenes. In this regard, insight into their interactions with metal ions helps us to understand MXene evolution from MAX precursors and may suggest ways to optimize their synthesis.

Over the years of research on MXenes, interactions with metal ions have been discovered and utilized, and have played crucial roles in many aspects, ranging from synthesis and processing to structure design and various applications. However, some scientific questions have not been answered, such as the different effects of metal ions on MXene structure control. Therefore, a timely review of the interaction between metal ions and MXenes is needed. This review classifies the different effects of metal ions on MXenes into three categories: intercalation, crosslinking, and etching (Figure 1). The roles metal ions play in MXene synthesis, and processing are emphasized, and the ways they change its properties, structure, and surface chemistry are also discussed. The fundamental chemistry and the mechanisms of different effects or behaviors are discussed, including ion exchange, interlayer expansion, aggregation, gelation, and defect formation. Research progress on the roles metal ions have in specific cases, such as supercapacitors, metal-ion batteries, catalysis, and water treatment, is then considered, and finally, some possible future developments are highlighted.

2. Different Roles of Metal Ions in MXene Synthesis and Processing

In the MXene development, metal ions play key roles in the synthesis and processing, such as MXene delamination, surface modification, structure control, property altering, MXene composite construction. The various roles are attributed to their interactions with MXenes and the unique nature of MXenes. In general, chemical interactions between guest ions and host layer solids include electrostatic interactions, charge transfer effects,
2.1. Metal Ion Intercalation

2.1.1. Intercalation in MXene Synthesis

Unlike van der Waals forces between the graphenes in graphite, there are metallic M-A bonds between the MXene layers in the MAX phase, which are hard to break by mechanical forces. Therefore, chemical (electro-chemical) reactions are necessary, and oxidizing etchants that react with the A layers in MAX are generally used. Additional intercalation is also required to obtain single or few-layer MXene sheets. The first report of the synthesis of the MXene, Ti$_3$C$_2$T$_x$, was in 2011, where it was produced by immersing a Ti$_3$AlC$_2$ precursor in a HF solution, where the selective etching of Al layers resulted in a graphene-like structure, and certain terminations (-O, -OH, and/or -F) were introduced on the surface. The obtained MXene (HF-MXene) could be spontaneously intercalated with organic molecules (e.g., dimethyl sulfoxide, urea) and cations (e.g., Li$^+$, Na$^+$, K$^+$). Given this post-intercalation ability, a one-step and milder synthesis route was proposed in 2014, using a mixture of hydrochloric acid (HCl) and lithium fluoride salt (LiF) as the etchant. Compared with HF-MXene, a dramatic change in the c-lattice parameter (c-LP, including the thickness of two MXene flakes and their interlayer spacing) with Li$^+$ intercalation was observed, causing easier delamination and fewer defects.

It has been shown that the cation intercalation during etching process plays a vital role in the synthesis, in addition to the formation of HF. As illustrated in Figure 2a, H$_2$O molecules occupy some of the Ti$_3$C$_2$ interlayer space, after the removal of Al atoms by the HF solution. Only a small number of cations (M$^{n+}$) can be intercalated with an uneven distribution (M@Ti$_3$C$_2$-I, Figure 2a), and thus a small structural change is produced. In contrast, if the etching and M$^{n+}$ ion intercalation are carried out simultaneously, the hydrated cations are evenly distributed between the layers, resulting in a larger interlayer spacing which facilitates exfoliation (M@Ti$_3$C$_2$-II, Figure 2a). This is shown by the XRD patterns in Figure 2b. When HF-Ti$_3$C$_2$ is intercalated with LiCl, NaCl or SnCl$_4$·5H$_2$O (i.e., Li@Ti$_3$C$_2$-I, Na@Ti$_3$C$_2$-I, or Sn@Ti$_3$C$_2$-I), there is only a slight shift of the (0002) peak from its original position at 8.91°. However, when HF/LiCl, HF/NaCl or HF/SnCl$_4$ is proposed in 2014, using a mixture of hydrochloric acid (HCl) and lithium fluoride salt (LiF) as the etchant. Compared with the controlled formation of HF, the combined effect improves the reaction kinetics resulting in the complete conversion of Ti$_3$AlC$_2$ to Ti$_3$C$_2$T$_x$ (Figure 2c) and accelerates the H$_2$O uptake during washing to facilitate delamination. Thus, shaking by hand is enough to obtain monolayer MXene, instead of sonication or additional delamination. The obtained flakes have large lateral dimensions (4–15 μm) and a uniform thickness (∼2.7 nm), as shown in Figure 2d. Compared with the calculated thickness of a single layer (0.98 nm), the increased thickness measured by AFM is due to surface adsorbates, such as water molecules. Moreover, the MXene flakes produced using Route 2 show well-defined and clean edges with a much lower defect concentration in high-resolution TEM images, resulting in better electronic properties.
2.1.2. Intercalation in MXene Processing

It is well known that intercalation is an effective way to alter the physical and chemical properties of 2D materials, including the band gap, conductivity, optical and mechanical properties, chemical reactivity, etc. A larger interlayer spacing increases ion diffusion and exposes more active sites, significantly improving the electrochemical performance. MXenes prepared by the LiF/HCl or HF/LiCl method can be intercalated with various other metal cations, including univalent ions (e.g., Na\(^{+}\), K\(^{+}\)) and multivalent ions (e.g., Be\(^{2+}\), Ca\(^{2+}\), Mg\(^{2+}\), Zn\(^{2+}\), Mn\(^{2+}\), In\(^{3+}\), Ho\(^{3+}\), Al\(^{3+}\)). After immersing the MXenes in different salt solutions, intercalants remain in the interlayer space due to electrostatic interactions (Figure 3a) and therefore increase it. The interlayer expansion is different for different metal ions. Li et al. prepared metal ion (M\(^{n+}\)) intercalated Ti\(_3\)C\(_2\)T\(_x\) MXene electrodes (M\(^{n+}\)-MXene) with controllable interlayer spacings. As shown in Figure 3b,c, the (0002) peak shifted to a lower angle, from 6.7\(^{\circ}\) (neat MXene produced by LiF/HCl etching) to 5.9\(^{\circ}\) (Ca\(^{2+}\)-MXene), 5.9\(^{\circ}\) (Mg\(^{2+}\)-MXene), 5.6\(^{\circ}\) (Al\(^{3+}\)-MXene), 5.9\(^{\circ}\) (Ho\(^{3+}\)-MXene), 5.8\(^{\circ}\) (In\(^{3+}\)-MXene), and 5.7\(^{\circ}\) (Be\(^{2+}\)-MXene), corresponding to expanded d-spacings (equal to c-LP/2) of 13.2, 14.7, 15.0, 15.6, 15.3, 15.2, and 15.1 Å, respectively. The change in d-spacing is explained by the intercalation chemistry and the related

Figure 2. The effect of metal ion intercalation in MXene synthesis. a) Schematic of metal ion intercalation in MXene synthesis. Route 1: the molar ratio of LiF and Ti\(_3\)AlC\(_2\) is 5:1; Route 2: the molar ratio of LiF and Ti\(_3\)AlC\(_2\) is 7.5:1. The inset SEM image is multilayer Ti\(_3\)C\(_2\)T\(_x\) prepared by HF etching. The inset TEM images are Ti\(_3\)C\(_2\)T\(_x\) flakes produced by Route 1 and 2. Left-hand side: Reproduced with permission.[7] Copyright 2011, Wiley-VCH. Right-hand side: Reproduced with permission.[40] Copyright 2016, Wiley-VCH. b) XRD patterns of M@Ti\(_3\)C\(_2\)-I and M@Ti\(_3\)C\(_2\)-II. Reproduced with permission.[39] Copyright 2020, Elsevier. c) XRD patterns of Ti\(_3\)C\(_2\)T\(_x\) MXene prepared by Route 1 and Route 2. d) AFM height profiles of Ti\(_3\)C\(_2\)T\(_x\) flakes produced by Route 1 and 2. Those produced by Route 2 have the same height of ≈2.7 nm and are identified as monolayers. Reproduced with permission.[40] Copyright 2016, Wiley-VCH.
hydrated radius of metal ion, which will be explained in the next section. As expected, the M\(^{\text{III}}\)-MXene electrodes have an almost negligible interfacial resistance with the electrolyte, indicating that the charge-transfer and ion diffusion are increased by the presence of the intercalants.

Apart from the interlayer spacing, the mechanical properties, electrical conductivity, and stability of MXenes are also influenced.\(^{[27,44,45]}\) The introduction of intercalants (e.g., Li\(^+\), dimethylsulfoxide, and tetraethylammonium hydroxide) is thought to result in a lower conductivity, worse mechanical properties, and instability.\(^{[27,46]}\) Removing the intercalants by cation exchange in an acid solution\(^{[46]}\) or annealing\(^{[47]}\) can significantly increase the electrical conductivity. However, Osti et al. found that K\(^+\) intercalation improved stability and structural homogeneity, and decreased the mobility of water confined between layers.\(^{[48]}\) It was also shown by Ding et al. that the intercalation of Al\(^{3+}\) ions improved the stability of a Ti\(_3\)C\(_2\)T\(_x\) membrane in aqueous solution and there was no structural collapse after long-time soaking in water.\(^{[49]}\) An increase in the tensile strength of a Ti\(_3\)C\(_2\)T\(_x\) film produced by Al\(^{3+}\) intercalation was reported by Liu et al., while the intrinsic electrical conductivity was maintained.\(^{[50]}\) Therefore, more research is needed to clarify the effects of metal ion intercalation on the mechanical properties, electrical conductivity, and stability of MXenes.

The effect of intercalation on the electronic structure and surface chemistry has also been investigated. Using X-ray absorption spectroscopy (XAS), Al-Temiey et al. found that cation intercalation (Li\(^+\), Na\(^+\), K\(^+\), and Mg\(^{2+}\)) strongly affected the oxidation state of the Ti atoms in Ti\(_3\)C\(_2\)T\(_x\) MXene after drying in air, while H\(_2\)SO\(_4\) pre-treatment prevented it.\(^{[51]}\) Combining XAS with X-ray photoemission electron microscopy (X-PEEM), the Ti oxidation states of Li\(^+\)- and Mg-TiC\(_2\)T\(_x\) were found to depend on their thickness, while those of Na\(^+\)- and K-TiC\(_2\)T\(_x\) did not.\(^{[52]}\) This difference is related to many factors, such as the probing depth, the particle geometry, and the amount of water confined in the MXene layers under different pressures. Overall, the impact of the intercalation of different metal ions on MXene properties differs and this requires further investigation. Furthermore, metal cation intercalation in alkali solutions may lead to a larger d-spacing\(^{[53]}\) than in neutral solutions and to a change in surface terminations.\(^{[53]}\) Halim et al. showed that F\(^-\) terminations (from 1.0 to 0.7 moles per mole of Ti\(_3\)C\(_2\)T\(_x\)) produced by fluoride etchants during MXene synthesis were replaced by -O terminations (from 0.5 to 1.2 moles; -OH, from 0.4 to 0.5 moles per mole of Ti\(_3\)C\(_2\)T\(_x\)) after NaOH treatment.\(^{[54]}\)

### 2.1.3. The Intercalation Mechanism

As mentioned above, metal ion intercalation significantly weakens the interaction between layers, which helps overcome the sluggish exfoliation kinetics during the synthesis and alters the physical and chemical properties of MXenes. During the initial Ti\(_3\)C\(_2\) exfoliation step in a HF solution, the strong bonding between Ti and F atoms weakens the Ti-Al bonds, which permits HF molecular intercalation into Ti\(_3\)AlC\(_2\) to etch Al atoms by forming AlF\(_3\) and H\(_2\), accompanied by Ti-F bond formation. With the Ti\(_3\)C\(_2\) layer isolation, H\(_2\)O molecules penetrate the interlayer space to support the exfoliation process by delaminating the Ti\(_3\)C\(_2\)T\(_x\) and forming -OH/O terminations the resulting surfaces.\(^{[55]}\) In most cases, the H\(_2\)O intercalation is promoted by the hydration of metal ions due to the strong electrostatic interactions between the negatively charged Ti\(_3\)C\(_2\)T\(_x\) surface and metal cations, in contrast with the considerably weaker interaction with pure H\(_2\)O.\(^{[27]}\) The zeta potential of the Ti\(_3\)C\(_2\)T\(_x\) dispersion is lower than −30 mV over a wide pH range,\(^{[56,57]}\) which explains why the sluggish exfoliation kinetics is hastened by metal ion intercalation in the HF/Li and LiF/HCl methods.

The mechanism of the intercalation of various metal ions by immersing MXene in different salt solutions has also been investigated. Sharma et al. found by ICP-MS measurements that the clay-like (Li\(^{+}\)-intercalated) Ti\(_3\)C\(_2\)T\(_x\) released Li\(^+\) and H\(^+\) ions and took up K\(^+\) and Na\(^+\) ions, when immersed in 1 m KCl and 1 m NaCl, respectively.\(^{[58]}\) However, no ion exchange occurred in 1 m LiCl, with almost zero driving force (Figure 4a). The ion exchange process is complex, and is controlled by kinetic and thermodynamic factors. With immersion calorimetry, the K\(^+\)-Li\(^+\) exchange and Li\(^+\) de-intercalation are exothermic, while Na\(^+\)-Li\(^+\) exchange

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**Figure 3.** The effect of metal ion intercalation in MXene processing. a) EDS element mapping of Al\(^{3+}\)-MXene, Mg\(^{2+}\)-MXene, Ca\(^{2+}\)-MXene, and Ho\(^{3+}\)-MXene. The MXene here is Ti\(_3\)C\(_2\)T\(_x\). b) XRD patterns of neat MXene, Ca\(^{2+}\)-MXene, Mg\(^{2+}\)-MXene, and Al\(^{3+}\)-MXene under 75% relative humidity at room temperature. c) XRD patterns of Be\(^{2+}\)-MXene, In\(^{3+}\)-MXene, Ho\(^{3+}\)-MXene, and neat MXene. Metal ion intercalation enlarges the interlayer spacing. Reproduced with permission.\(^{[42]}\) Copyright 2020, Wiley-VCH.
The mechanism of metal ion intercalation. a) Illustration of ion exchange in a clay-like MXene. The ion exchange is generally thought to occur between the solution and ions located between the MXene layers, accompanied by $H^+$ release. Reproduced with permission. [58] Copyright 2017, American Chemical Society. b) Correlation of the interlayer spacing of $M^{n+}$-MXene (including $Ca^{2+}$, $Mg^{2+}$, $Ho^{3+}$, $In^{3+}$, $Be^{2+}$, and $Al^{3+}$) electrodes and the hydrated radius of intercalated metal ions (obtained from Marcus’s group). Reproduced with permission. [42] Copyright 2020, Wiley-VCH. c) XRD patterns of ion-intercalated $Ti_3C_2T_x$ MXene with humidity control. Reproduced with permission. [38] Copyright 2016, American Chemical Society. d) $Li^+$, $Cs^+$, and $Mg^{2+}$ representative atomic arrangements around different cations confined in two $Ti_3C_2T_x$ layers. Reproduced with permission. [60] Copyright 2020, Royal Society of Chemistry. e) $^{23}Na$ NMR spectrum to investigate the mechanism of $Na^+$ intercalation into $Ti_3C_2T_x$ during electrochemical cycling. Reproduced with permission. [67] Copyright 2016, American Chemical Society.

is endothermic. The greater extent of the $Na^+$-$Li^+$ exchange is due to the higher ion mobility. The effect of the intercalation of different ions has been addressed, especially the effect on interlayer spacing as shown in Figure 3b, which is supposed to be related to the hydration state of the cations. A larger d-spacing is caused by the intercalated metal ion of a larger hydrated radius (Figure 4b). Moreover, the interlayer spacing is found to change with the humidity level on account of the $H_2O$ uptake or loss. Using in situ XRD and thermogravimetric analysis, Ghidiu et al. suggested that the expansion was related to the hydration enthalpy of the cations (Figure 4c). [18] A cation with a higher charge/radius ratio tends to have a higher absolute value of hydration enthalpy, [39] suggesting a tendency to form a bilayer $H_2O$ structure between layers at lower humidity. Thus, $Li^+$ and $Na^+$-MXene start to expand at ≈90% relative humidity (RH), while $Mg^{2+}$-MXene responds at ≈10% RH.

The specific intercalation states and interfacial chemistry of different metal ions between two MXene sheets have been tracked, which helps provide a deeper understanding of MXene energy storage properties and processes. Gao et al. used $ab initio$ molecular dynamics (AIMD) simulations to investigate the atomic arrangements around $Li^+$, $Na^+$, $K^+$, $Cs^+$, and $Mg^{2+}$ confined in two $Ti_3C_2T_x$ MXene layers (Figure 4d). [60] As previously reported, there was a certain number of water molecules around each cation, while the hydrated cations had different locations between the MXene layers. $Li^+$, $Na^+$, and $K^+$ prefer to be on the surface, while $Cs^+$ and $Mg^{2+}$ prefer to be between the layers. Radial distribution functions (RDF) quantified the relative position between -O surface termination (O-T) and cations. The capacitance at the open circuit potential (OCP) was measured to be in inverse proportion to this cation-O-T distance. Considering the effect of water molecules confined between MXene layers, a modified electric double layer (EDL) model was proposed to explain this relationship. At the same time, the EDL energy storage mechanism was identified in the neutral aqueous electrolytes, which will be discussed later in detail.

Understanding intercalation chemistry in a nonaqueous system is also essential, especially during the electrochemical process. Metal cations, also the charge carriers, intercalate and...
de-intercalate the MXene layers to achieve energy storage and release, and the state of the intercalated ions needs to be understood. [61–63] Kajiyama et al. used solid-state 23Na NMR to reveal the Na+ intercalation mechanism. As presented in Figure 4e, 3 different Na+ signals can be detected, representing solvated Na+ from the residual electrolyte, solvated Na+ trapped in the SEI layer or adsorbed on the surface, and completely or partially de-solvated Na+ intercalation. It is believed that de-solvated Na+ intercalation is the main contributor to energy storage. Furthermore, the solvent effect has also been investigated. Wang et al. demonstrated Li+ intercalation with a complete de-solvation behavior in a propylene carbonate (PC) system. However, solvent co-intercalation occurs in acetonitrile (ACN) and dimethylsulfoxide (DMSO) systems. [64] Remarkably, the efficient de-solvation in PC results in a high volumetric capability. The interaction between intercalated ions and the MXene surface is supposed to determine the electrochemical behavior of MXenes during charging. [65, 66] Regrettfully, few studies have focused on intercalation chemistry in a nonaqueous system, and more attention needs to be paid to this subject.

### 2.2. Metal Ions as Crosslinking Agents

#### 2.2.1. Crosslinking in MXene Processing

The addition of a metal salt solution can alter the stability of Ti3C2Tx colloidal suspensions, and flocculation or gelation occurs due to the destruction of electrostatic repulsive forces between the sheets. The treatment with alkali metal hydroxides (e.g., NaOH, KOH) can result in Ti3C2Tx nanosheet aggregation and a crumpled structure, with the intercalation of metal ions. [28, 68–70] A 3D nanoribbon structure can be fabricated using an increased alkali concentration. [71–73] A high concentration NaCl solution was also found to induce a crumpled morphology. Interestingly, some multivalent metal ions (e.g., Fe2+, Mg2+, Co2+, Ni2+, Al3+, and K+) induce Ti3C2Tx nanosheet crosslinking to form a stable 3D hydrogel, rather than simple flocculation or aggregation (Figure 5a, b). [28] The gelation process is accomplished in minutes when the MXene concentration is high enough (≥ 6 mg mL−1). The MXene concentration is a key factor, as only flocculation occurs in low concentration, because of the limited interaction.
range and fast charge neutralization of metal ions. Following this, Ding et al. fabricated a 3D Ti₃C₂Tₓ MXene aerogel by Mg²⁺ crosslinking, without polymeric binders or templates.[58] Using the thermal contraction of polystyrene (PS) substrate, a crumpled-textured Ti₃C₂Tₓ coating (CT-MXene) was pre-prepared. This CT-MXene allows a higher Mg²⁺ loading, and which induces gelation on the surface after soaking in a Ti₃C₂Tₓ dispersion (21 mg mL⁻¹), as illustrated in Figure 5c. The (0002) peak shift indicates that the Mg²⁺ ions are intercalated. The aerogel formed is really tough because of the strong crosslinking, so that the pore structure is preserved even after the intercalated Mg²⁺ is removed by acid rinsing with only a slight change in specific surface areas (from 140.5 to 131.0 m² g⁻¹, Figure 5d). The aerogel remained intact under ultrasonication in water, in contrast to the quick destruction of the aerogel without Mg²⁺ crosslinking (Figure 5e). The strong interaction also ensures better inter-sheet connections and uninterrupted electron diffusion paths, indicated by the aerogel having a higher electronic conductivity (758.4 ± 41.6 S m⁻¹) than the original (471.3 ± 22.8 S m⁻¹, Figure 5f). Lin et al. fabricated highly stable Ti₃C₂Tₓ foams by placing the metal substrate (Zn, Al, Fe, Co, and Ni) to an acidic MXene or MXene/GO hybrid dispersion, where the metal ions diffuse out and induce gelation.[74] Large pore size and thick lamellas tend to form in a higher ion concentration and a quicker assembly process by pH control. The prepared foams can be loaded with different nanoparticles (SiO₂ and Fe₃O₃).

2.2.2. The Crosslinking Mechanism

Before introducing the crosslinking behavior of metal ions, the aggregation of MXene flakes in alkali metal hydroxides and salt solutions of high concentration will be explained first.[75–77] The main reason is the imbalance between electrostatic attraction and electrostatic repulsion.[69,78] The OH⁻ in alkali metal hydroxides (e.g., NaOH) passivate the positively charged edge sites of Ti₃C₂Tₓ, while Na⁺ is adsorbed on the negatively charged surface sites. The positive Na⁺ ions attract the adjacent MXene nanosheets, which results in a large number of face-to-face interactions between them. In the case of a salt solution, the Debye length decreases with the increased salt concentration, which indicates that the repulsion between the nanosheets is reduced, creating a face-to-face interaction between them.[79] This strong interaction causes the nanosheet aggregation and a crumpled structure after drying, which may also account for the nanoribbons formed in high concentration alkali metal hydroxides, as mentioned earlier. The high concentration of OH⁻ may over-passivate the edge making it negatively charged. Meanwhile, the increased concentration of Na⁺, which prefers to be absorbed on the surface, attracts the negatively charged edge. Such a plane face-to-edge attraction induces the high-degree of folding and crumpling of the MXene sheet, and thus nanoribbons are formed. This process is like rolling a sheet of paper into a tube-shape from one edge side.

Compared with aggregation and intercalation, the direct chemical or ionic bonding between multivalent metal ions (e.g., Fe²⁺, Mg²⁺, Co²⁺, Ni²⁺, Mg²⁺, Al³⁺) and surface terminations is greater in the crosslinking. Giving the Ti₃C₂Tₓ gelation process with Fe²⁺ ions as an example. Firstly, the electrostatic interactions with Fe²⁺ ions and negatively charged Ti₃C₂Tₓ sheets break the original electrostatic balance among sheets. Then, as linkers, the ions interact with -OH/-O and -F groups on MXene surface.[28] In this process, the hydration shells around Fe²⁺ are destroyed, as obvious Fe-O and Fe-F bonds (very low intensity) are detected in in XPS spectra (Figure 6a,b). What is more, the increase in inter-layer spacing is only ±0.12 nm, close to the bare ionic radius of Fe²⁺ without the hydration shell.[74] The crosslinking mechanism with Zn²⁺ ions is also revealed by XAS, where the electronic structure and local environments of Ti and Zn is investigated.[74] The normalized Ti K-edge XANES spectra in Figure 6c indicated that no obvious MXene degradation occurred, as the signal of Zn²⁺-MXene resembled that of the original MXene but differed from that of TiO₂. The Zn K-edge XANES spectrum of Zn²⁺-MXene is similar to that of ZnSO₄, indicating the zinc is in the Zn²⁺ ionic state. Moreover, Zn-O complexes with an atomic dispersion on MXene are the primary interaction form, as exhibited in Figure 6d, and XPS results confirm the Zn-O ionic bonding. The above results show that the strong electrostatic interactions between multivalent metal ions and negatively charged terminations of adjacent MXene flakes break the shielding effect of hydration layer, which allow the ionic bonding to form. Meanwhile, the high concentration of MXene sheets provides more interaction chances and helps the formation of crosslinking network. However, the research on the crosslinking mechanism is still scarce until now, and more investigations are required, such as the effect of surface groups and MXene species.

2.3. The Crosslinking Mechanism

2.3.1. Etching Effect in MXene Synthesis

The molten salt route is becoming more important in MXene synthesis, in addition to the wet chemical etching route. In this approach, the metal ions (e.g., Cu²⁺, Zn²⁺, Cd²⁺, Co²⁺) act as the oxidant to etch the A layer (e.g., Si, Al) in the MAX phase.[12–14,80] For example, Ti, SiC₂ makes reactions with molten CuCl₂ at 750 °C and produces Ti₃C₂Cl₂, Cu clusters, and SiCl₄ gas. By coupling different MAX phases with appropriate molten salts (including cations and anions), a broad family of MXene materials can be theoretically synthesized, with different surface chemistries and structures. Similar to the HF route, Ti vacancies are also found, which indicates that the metal ions not only etch A atoms but also Ti atoms. Because of this, it is essential to study the interaction between metal ions and MXene during synthesis in molten salts.

It has been reported by Gu et al. that specific numbers of Ti vacancies are introduced by reacting Ti₁₋ₓAlₓC₂ with ZnCl₂ at 550 °C for 10 h, and, at the same time, Zn atoms are immobilized on the MXene layer (Figure 7a).[81] Similarly, Song et al. introduced Ti defects by etching Ti₁₋ₓAlₓN in molten CuCl₂ (the molar ratio of MAX to salt was 1:2) at 1000 °C for 7 h, or in molten CoCl₂ (800 °C, 7 h).[82] After the reaction, the products were treated with a HCl solution and FeCl₃ to remove Cu particles, or only a HCl solution to remove Co particles. The final products had a visible layered structure with a Cu content of 1.8 at% (Figure 7b). A Ti vacancy marked by a red circle in the HAADF-STEM images was observed, and the lattice mismatch of Ti atoms is indicated by the white ellipse. Cu single atoms with a valence state between 0
and +2 were also detected, as indicated in the XANES results. In addition to the Ti vacancies and anchoring of single atom metals, in-plane pores were also generated by etching the MAX precursor in molten salts. Zhang et al. found that Ti$_3$C$_2$Cl$_2$ with in-plane pores was synthesized by reacting Ti$_3$AlC$_2$ with a NaCl/ZnCl$_2$ salt mixture at 550 °C for 5 h.\cite{83} With an increasing mole fraction of NaCl, the micropores gradually evolved into mesopores (3–4 nm), and a specific surface area of 85 m$^2$ g$^{-1}$ was achieved.

### 2.3.2. Etching Effect in MXene Processing

For MXenes prepared by wet chemical etching, similar effects can be achieved by post-processing with salt solutions. As illustrated in Figure 7c, single copper atoms can be anchored on Ti$_3$C$_2$T$_x$ sheets by slowly adding a certain amount of CuCl$_2$·2H$_2$O (1 mg mL$^{-1}$; 0.67 mL) to a Ti$_3$C$_2$T$_x$ dispersion.\cite{84} No Cu peak was detected in the XRD pattern. The valence state of the Cu atom is calculated to be +0.42 from the XAS results, and uniform Cu single atoms on the Ti$_3$C$_2$T$_x$ lattice are observed as bright dots (Figure 7d). Cu single atoms and Cu nanoclusters formed when treated with a larger amount of CuCl$_2$·2H$_2$O (2.01 mL), are shown in the HAADF-STEM image (Figure 7d). The coordination conditions of the Cu are Cu-O and Cu-Cu, from the FT-EXAFS curves. Furthermore, by increasing the Cu$^{2+}$ concentration, Ti$_3$C$_2$T$_x$ degradation and in-plane etching occurred, as shown in Figure 7e.\cite{85,86} Porous Ti$_3$C$_2$T$_x$ flakes (pore size: ≈10 nm) were fabricated by Ren et al. by mixing a delaminated Ti$_3$C$_2$T$_x$ colloidal solution with a CuSO$_4$ solution, followed by acid washing (Figure 7f). During the process, the flakes were partially oxidized to TiO$_2$ which was removed by diluted HF acid (5 wt%). Not only Cu$^{2+}$ but many other metal ions such as Co$^{2+}$ and Fe$^{3+}$ have been reported to have etching ability. By controlling the concentration of Cu$^{2+}$, the pore size and density could also be changed. Xiong et al. found that a CuSO$_4$ concentration of 0.2 M generated pores ranging in diameter from 2 to 15 nm by later HF acid (5 wt%) treatment.\cite{87} A slightly higher concentration (0.4 M) produced a similar pore size but a higher pore density. When the concentration was increased to 1 M, the pore size increased, ranging from 15 to 25 nm.
Some other metal ions (e.g., Cd$^{2+}$, Ru$^{3+}$, Ag$^+$, AuCl$_4^{-}$, PdCl$_4^{-}$) are also self-reduced to lower or zero valence states when in contact with MXenes, in the absence of extra reagents. Peng et al. fabricated Ru-doped Mo$_2$CT$_x$ sheets by adding RuCl$_3$ to the MXene dispersion. It is thought that the Mo vacancies produced in the synthesis from Mo$_2$GaC initiate the reduction of Ru$^{3+}$ ions, accompanied by an increased oxidation state of the nearby Mo atoms. XAS and XPS results indicate that Ru atoms are introduced into the Mo$_2$CT$_x$ lattice and occupy the Mo sites without Mo-Ru bonding. In addition, a higher dose of RuCl$_3$ leads to Ru nanoparticles forming on the surface. Satheeshkumar et al. directly deposited Ag, Au, and Pd nanoparticles onto the Ti$_3$C$_2$T$_x$ surface, by adding the corresponding salts (AgNO$_3$, HAuCl$_4$, and PdCl$_2$) to a MXene suspension. Peaks of Ag, Au, and Pd metals were detected in the XRD patterns. It was also reported by Xie et al. that visible metal layers formed on the surface after the MXene film was treated with water containing Ag$^+$ or AuCl$_4^{-}$ ions.

### 2.3.3. The Etching Mechanism

The interaction between metal ions and MXenes can generate in-plane defects (vacancies and pores) and may even degrade the MXenes. Simultaneously, the valence state of the metal ions is reduced, and even zero valent metals (e.g., Ag, Au, Pt) can be...
Figure 8. The mechanism of metal ion etching. a) A diagram of the anchoring of single metal atoms on Ti vacancies during molten salt etching. Reproduced with permission.[82] Copyright 2021, Elsevier. b,c) High-resolution Cr 2p and Ti 2p XPS spectra of Ti3C2Tx-based films before and after HCrO4− removal. The valence state of Cr in HCrO4− is reduced from Cr(VI) to Cr(III), accompanied by a valence state increase of Ti in Ti3C2Tx. d) Differences in charge density of HCrO4− on O- and OH-terminated Ti3C2. The turquoise and yellow regions indicate depletion and accumulation of electrons, respectively. Reproduced with permission.[89] Copyright 2019, Springer Nature. e) Schematic illustration of U(VI) removal at different pH values. Reprinted with permission.[88] Copyright 2018, American Chemical Society.

As mentioned earlier, in-plane pores on Ti3C2Tx flake are prepared with molten NaCl/ZnCl2 salt mixtures as etchants during the synthesis. A pore preserving mechanism was proposed by Zhang et al. to explain the pore formation.[83] Different from the mechanism that vacancies caused by molten salt etching, they thought the defects present after etching were derived from precursor's original structural/crystal defects. The pores could be well preserved with the physical support of the larger individual crystals (e.g., NaCl) during cooling. Otherwise, they would collapse and disappear after cooling if only ZnCl2 is used.

The reasons for the reduction of metal ions and the in-plane pore generation in MXenes during post-processing have also been studied. Ti3C2Tx can be oxidized to TiO2 in Cu2+ solutions as mentioned above. Ren et al. believed that the real oxidant is the dissolved O2 in water, while the Cu2+ cations act as catalysts.[85] However, a charge transfer mechanism has been proposed by Xie et al., where the reduction of metal ions is accompanied by valence state changes of Ti in Ti3C2Tx.[89] Ti3C2Tx-based films were fabricated to remove heavy metal ions, and both negatively and positively charged ions were found to have significant removal efficiency, which rules out simple adsorption with electrostatic interactions. With the HCrO4− removal, the interlayer spacing of Ti3C2Tx is increased and the material becomes disordered, suggesting the intercalation of Cr species. It is interesting to find the coexistence of Cr(VI) and Cr(III) species, with a high percentage (up to 82%) for Cr(III) (Figure 8b). Meanwhile, an increased fraction of Ti(IV)-O is found by fitting the XPS spectra (Figure 8c), meaning the electron loss from Ti3C2Tx. It is reasonably
3. Metal Ions in MXene Applications

3.1. Applications in Supercapacitors

MXenes are promising electrode materials in supercapacitors, with superhigh volumetric and gravimetric capacitance (up to \( \approx 1500 \text{ F cm}^{-1} \) and \( \approx 400 \text{ F g}^{-1} \), respectively).\[99,100\] Due to their superior flexibility, optical properties, and electronic conductivity, they are suitable for fabrication into various supercapacitor devices, such as micro-supercapacitors\[101–103\] and transparent solid-state supercapacitors.\[104,105\] It has been demonstrated that various cations can be electrochemically reversibly intercalated into MXene and occupy active sites to participate in energy storage. For MXenes, ions are normally adsorbed on the edges or the outer surface of the particle firstly, and then intercalated into layers. The intercalated ions are always accompanied by a hydrated shell in aqueous electrolytes, and this causes an increase in the interlayer spacing of MXene, while an increased electrostatic attraction between the Ti\(_3\)C\(_2\)T\(_x\) sheets and intercalated cations during discharging leads to a contraction instead. The response of electrodes, which is determined by the competition between contraction and expansion, differs with different metal ions.\[106–107\] For electrode materials, zero deformation is preferred to maintain the electrode structure and achieve a prolonged lifetime and stable cycling.

MXenes store charges by ion adsorption and intercalation, and the charge storage capacitance is dominated by the specific charge storage mechanism. MXenes are regarded as intrinsically pseudo-capacitive materials, due to their surface chemistry and layered structure. However, the charge storage mechanism can be related to EDL (i.e., electrostatic interactions) or pseudo-capacitive one (i.e., surface redox reaction or intercalation), or a combination of both, which depends on electrolyte components. In acidic electrolytes (e.g., H\(_2\)SO\(_4\)), a pseudo-capacitive mechanism is recognized. Measurements for Ti\(_3\)C\(_2\)T\(_x\) in H\(_2\)SO\(_4\) have shown that the reduced oxidation state of Ti changes with the protonation of oxygen functional groups:\[109,110\]

\[
\text{Ti}_3\text{C}_2\text{O}_x\text{(OH)F}_z + 1/2\text{e}^- + 1/2\text{Zn}^{2+} \rightarrow \text{Ti}_3\text{C}_2\text{O}_{1/2x}\text{(OH)}_{1/2z} \text{F}_z
\]

(2)

The DFT calculations in Figure 9a indicate a linear relation between the Ti oxidation state change and the atomic Bader charge at different O/H ratios and electrode potential.\[111\] The number of active sites determines the pseudo-capacitance in H\(_2\)SO\(_4\), and an ultra-high capacitance of 1190 F g\(^{-1}\) is predicted for Ti\(_3\)C\(_2\)O\(_x\). At low reaction rate, there are minor differences between the ion adsorption and intercalation in H\(_2\)SO\(_4\). In neutral electrolytes (e.g., Li\(_2\)SO\(_4\), K\(_2\)SO\(_4\), MgSO\(_4\)), the EDL charge storage is the main contribution, no matter for ion adsorption and intercalation. The different mechanisms for H\(_2\)SO\(_4\) and for neutral electrolytes are induced by the strong interactions between water solvent molecules and cations. The hydrated shell is thought to hinder the orbital coupling of the intercalated or adsorbed cations with the MXenes.\[112\] For this reason, the pseudo-capacitive reaction cannot occur within the applicable potential window, resulting in solely EDL formation, even under confinement of MXene layers. Recently, the electrochemical behavior of Ti\(_3\)C\(_2\)T\(_x\) MXene in water-in-salt electrolytes (e.g., 19.8 m LiCl/H\(_2\)O) is reported. Separated sharp redox peaks in CV curves and an abrupt change of the interlayer spacing (11.0–12.9 Å) are observed. The diffusion-controlled (de-)intercalation of solvated cations causes these changes. This behavior is distinct from typical EDL or pseudocapacitive charge storage. Overall, more efforts are required for a fundamental understanding of charge storage in MXenes.

Pure MXene electrodes prepared by HF etching have an unsatisfactory performance in various electrolytes, including H\(_2\)SO\(_4\) (Figure 9b),\[122\] but by taking advantage of their interactions between metal ions, their potential can be realized. Cation intercalation during etching has proven to produce a significant improvement. The Ti\(_3\)C\(_2\)T\(_x\) synthesized in LiF/HCl has outstanding performance in a H\(_2\)SO\(_4\) solution, with a high capacitance of 900 F cm\(^{-1}\) at 2 mV s\(^{-1}\) and good rate handling ability (Figure 9b).\[137\] As mentioned earlier, Li\(^+\) intercalation improves the exfoliation kinetics. The obtained MXenes has a higher conductivity, larger interlayer spacing, and higher content of -O terminations, which together improve the intercalation and surface redox reaction pseudo-capacitance. Additionally, it is a common strategy to change the interlayer structure by ion pre-intercalation to expose more active sites and facilitate ion diffusion.\[141\] For example, MXene electrodes with controlled interlayer spacings are prepared by pre-intercalating various metal cations to match the size of the charge carriers in neutral electrolytes (Figure 9c).\[142\] As a result, Al\(^{3+}\)-MXene and Be\(^{2+}\)-MXene films have improved volumetric capacitances (C\(_v\)) of 351.09 F cm\(^{-3}\), and 330.7 F cm\(^{-3}\) at 20 mV s\(^{-1}\) in 1.0 m Li\(_2\)SO\(_4\), respectively. Compared with neat MXene, the Be\(^{2+}\)-MXene also has C\(_v\) increases of 16.4% in Na\(_2\)SO\(_4\), 19.2% in K\(_2\)SO\(_4\), and 30.1% in ZnSO\(_4\). Higher capacitance retention of 81.8% in K\(_2\)SO\(_4\) is presented at 200 mV s\(^{-1}\). The surface chemistry can also be changed to improve the capacitance. Typically, more oxygen-containing functional groups can be introduced on the MXenes surface by immersing them in...
metal hydroxide solutions.\textsuperscript{[112]} A high capacitance of 500 F g\textsuperscript{-1} at 1 mV s\textsuperscript{-1} was reported after K\textsuperscript{+} ion intercalation and calcination, where only -O functional groups terminate the surface.\textsuperscript{[53]}

A 3D MXene electrode can be fabricated to address the restacking problem of 2D nanosheets and shorten the mass transfer path by using the crosslinking of metal ions.\textsuperscript{[29]} A Ti\textsubscript{1}C\textsubscript{1}T\textsubscript{x} MXene hydrogel electrode prepared by Fe\textsuperscript{2+} crosslinking can achieve an excellent rate performance ($\approx 226$ F g\textsuperscript{-1}), and its typical pseudocapacitive behavior is well maintained at 1 V s\textsuperscript{-1}, as shown in Figure 9d.\textsuperscript{[28]} Ding et al. used a Mg\textsuperscript{2+}-MXene aerogel as electrodes and PVA/H\textsubscript{2}SO\textsubscript{4} as a gel electrolyte to construct quasi-solid state micro-supercapacitors.\textsuperscript{[68]} As a result, a high areal-specific capacitance (409.3 mF cm\textsuperscript{-2} at 5 mV s\textsuperscript{-1}) was obtained, as well as high areal energy densities (7.4–21.6 $\mu$Wh cm\textsuperscript{-2}) and high areal power densities (0.1–1.1 $\mu$W cm\textsuperscript{-2}). In addition, MXenes are regarded as ideal 2D supports to couple with other pseudocapacitive materials, and their interactions with metal ions help the fabrication of composite electrodes.\textsuperscript{[113,114]}

As illustrated in Figure 9e, a MnO\textsubscript{2}/Ti\textsubscript{1}C\textsubscript{1}T\textsubscript{x} composite is synthesized by impregnating Ti\textsubscript{1}C\textsubscript{1}T\textsubscript{x} MXene in a MnSO\textsubscript{4} solution, with KMnO\textsubscript{4} being reduced.\textsuperscript{[108]} After annealing, the composite electrode had a capacitance of 212.1 F g\textsuperscript{-1} at 1 A g\textsuperscript{-1}. Similarly, other composite electrodes have been extensively investigated, such as Ti\textsubscript{1}C\textsubscript{1}/MoS\textsubscript{2},\textsuperscript{[115]} Ti\textsubscript{1}C\textsubscript{1}/CuS,\textsuperscript{[116]} Ti\textsubscript{1}C\textsubscript{1}/FeOOH quantum dots,\textsuperscript{[117]} Ti\textsubscript{1}C\textsubscript{1}/NiCoFe-LDH,\textsuperscript{[118]} Ti\textsubscript{1}C\textsubscript{1}/NiFe-LDH,\textsuperscript{[119,120]} Ti\textsubscript{1}C\textsubscript{1}/Ni\textsubscript{3}S\textsubscript{2},\textsuperscript{[121]} Ti\textsubscript{1}C\textsubscript{1}/Fe\textsubscript{3}O\textsubscript{4},\textsuperscript{[122]} Ti\textsubscript{1}C\textsubscript{1}/Ni\textsubscript{3}CO\textsubscript{3}(OH)\textsubscript{2},\textsuperscript{[123]} etc.
3.2. Applications in Metal-Ion Batteries

Rechargeable lithium-ion batteries (LIBs) are one of the most significant energy storage devices, and are widely used in portable electronic devices and the new electric vehicles. The pursuit of higher energy densities and the limited lithium resources have promoted the exploration of new electrode materials and non-lithium-ion batteries, including sodium-ion batteries (SIBs), potassium-ion batteries (PIBs), calcium-ion batteries (CIBs), etc.\textsuperscript{[61]} MXenes are new materials that can accommodate the insertion of various metal ions between their layers. As electrode materials, they are predicted to provide remarkable theoretical capacities (e.g., 447.8 mAh g\textsuperscript{-1} for LIBs, 351.8 mAh g\textsuperscript{-1} for SIBs, 191.8 mAh g\textsuperscript{-1} for PIBs, 319.8 mAh g\textsuperscript{-1} for CIBs, based on bare Ti\textsubscript{3}C\textsubscript{2}).\textsuperscript{[124–130]} Given that the metal ions play a crucial role as charge carriers in metal-ion batteries (MIBs), their interactions with MXenes, especially in electrochemistry, become extremely important.

Given the preferred ion adsorption on the surface, M\textsubscript{x}X with a higher effective surface area is expected to provide higher gravimetric capacities than M\textsubscript{x}X\textsubscript{2} and M\textsubscript{x}X\textsubscript{3}.\textsuperscript{[129]} That is to say, compared with Ti\textsubscript{3}C\textsubscript{2} and Ti\textsubscript{4}C\textsubscript{3}, Ti\textsubscript{2}C has a higher theoretical gravimetric capacity.\textsuperscript{[61]} In addition, -OH and -F terminations are believed to block ion diffusion and lower the theoretical capacities, while -O functional groups provide additional capacity.\textsuperscript{[25,135]} For example, once terminated with -F or -OH, the theoretical capacity is reduced to 130 or 67 mAh g\textsuperscript{-1} for Li\textsuperscript{+} storage.\textsuperscript{[136]} The different theoretical specific capacities shown for different metal ions can be understood by referring to the maximum adatom content and the corresponding charge transfer, which determines the electronic properties after ion adsorption.\textsuperscript{[130]} Figure 10a illustrates the bonding charge density for adatoms on bare Ti\textsubscript{3}C\textsubscript{2} and the
charge transfer from adatoms to Ti$_3$C$_2$. It is calculated that the amount of charge transfer are 0.21 (Li), 0.40 (Na), 0.47 (K), and 1.31 e$^-$ (Ca), with the respective maximum adatom contents being 2.8, 2.2, 1.2, and 1. Moreover, the corresponding diffusion barriers are estimated to be 0.068 (Li), 0.096 (Na), 0.103 (K), and 0.118 (Ca) eV, which are much lower than that on graphite (0.3 eV for Li). These calculations indicate that MXenes are promising electrode materials with a high rate.

Experimentally, when used the anode materials in LIBs, multilayer Ti$_3$C$_2$ powders prepared by 10 wt% HF gives capacities of 225 mAh g$^{-1}$ at C/25, and 110 mAh g$^{-1}$ at 1 C.[62] To achieve satisfied performance with rational material designs, the investigation of ion storage mechanism is urgently needed. MXenes store ions by adsorption and intercalation, and generally show distorted rectangular CVs with small pairs of redox peaks. In organic electrolytes, partially or completely de-solvation of cations occurs at the MXene-electrolyte interface or in intercalation, due to the lower solvation energy than hydration. The solvents would decompose and solid electrolyte interface (SEI) forms under the wide potential window. In most cases, those cations adsorbed on the MXene surface have solvation shells, and the complete charge separation results in EDL storage. However, those intercalated cations are usually partially or fully de-solvated, and a donor band forms due to the orbital overlap with a close contact of MXene-cation. This orbital hybridization allows charge transfer between MXenes and intercalated cations, and enhances the capacity. In 1.0 m LiPF$_6$-ethylene carbonate/dimethyl carbonate (LiPF$_6$-EC/DMC), a reversible interlayer spacing change (9.4–9.8 Å) is found, which is caused by the partially de-solvated Li$^+$ (de-)intercalation.[62] At the same time, a reversible reduction/oxidation of Ti of Ti$_3$CT$_x$ is caused. As mentioned in section 2.1.3, the PC solvent enables a fully de-solvated ion intercalation, and the increased intercalated ion number (0.93 Li$^+$ per Ti$_3$C$_2$T$_x$) leads to a higher capacity. In 1 m NaPF$_6$-ethylene carbonate/diethyl carbonate (NaPF$_6$-EC/DEC), the layered Ti$_3$C$_2$T$_x$ has a capacity of 270 mAh g$^{-1}$ at 20 mA g$^{-1}$ for the Na$^+$ intercalation/adsorption and a good cycle stability (100 mAh g$^{-1}$ over 100 cycles) the first few cycles.[67] Electrolyte decomposition is the main reason for the irreversible capacity in these cycles. A combination of XRD and TEM, shows that the interlayer spacing increases from 0.97 to 1.20 nm during the first sodiation, and remains unchanged in the next de-sodiation and the second sodiation (Figure 10b). This Na$^+$ pillar ing effect helps subsequent (de-)intercalation of de-solvated Na$^+$ and result in a stable cycling.

Similar to their use in supercapacitors, the use of MXene hybrid materials is another common way to provide a highly conductive framework for high-capacity active materials.[146] For example, through the adsorption of Sn$^{2+}$ on Ti$_3$C$_2$ sheets, SnO$_x$@Ti$_3$C$_2$ anode was prepared by a hydrothermal reaction, which had a much higher Li-storage capacity of ≈450 mAh g$^{-1}$ than SnO (≈63 mAh g$^{-1}$) and Ti$_3$C$_2$ anodes.[139] As illustrated in Figure 10f, NiCo-LDH materials were loaded on crumpled MXene, by introducing Ni$^{2+}$, Co$^{2+}$, and urea to an alkaline Ti$_3$C$_2$ suspension, followed by hydrothermal treatment.[136] Then Ti$_3$C$_2$/NiCoP composite was then prepared by phosphorylation with NaH$_2$PO$_4$. When used as the anode material in SIBs, it retained a specific capacity of 261.7 mAh g$^{-1}$ at 1 A g$^{-1}$ after 2000 cycles. Zhou et al. used the self-reduction of Ag$^+$ on MXene form a Ti$_3$C$_2$-Ag hybrid, which had an extraordinary long cycle lifetime (>5000 cycles) with a high Li-storage capacity of 310 mAh g$^{-1}$ at 1 C, as well as a good rate performance (150 mAh g$^{-1}$ at 50 C).[147] Other hybrid electrodes have been fabricated for MBs, such as Ti$_3$C$_2$/Fe$_3$O$_4$.[148–151] Ti$_3$C$_2$/W-doped Nb$_2$O$_5$.[152] Ti$_3$C$_2$/MoO$_3$.[153] and Ti$_3$C$_2$/GeO$_2$.[154] for LIBs, and Ti$_3$C$_2$/FeS$_2$.[155] Ti$_3$C$_2$/SnO$_2$.[156] Ti$_3$C$_2$/CoNiO$_2$.[157] and Ti$_3$C$_2$/SnS$_2$.[158] for SIBs, etc.

In recent years, MXene based metal ion hybrid capacitors (MICs) are attracting increasing research attention, due to the
advantages of both high energy density and power density. This kind of device is composed of one battery-type electrode and the other capacitor-type electrode. In most cases, the battery-type redox reaction occurs on the anode side, and capacitive reaction occurs on the cathode side. Sometimes, there is a reverse situation, and it depends on the potentials of the two reactions. As introduced before, MXenes demonstrate excellent ion storage performance, so they can be anodes in MICs. Luo et al. fabricated pre-intercalated Ti3C2 MXene (CTAB-Sn(IV)@Ti3C2) with cetyltrimethylammonium bromide (CTAB) and Sn⁴⁺ pillaring. When coupling the CTAB-Sn(IV)@Ti3C2 anode and activated carbon (AC) cathode, the lithium-ion hybrid capacitor (LIC) displayed the specific capacitance of 268 F g⁻¹ at 0.2 A g⁻¹ (based on the anode mass), and good capacity retention of 71.1% after 4000 cycles at 2 A g⁻¹. Fan et al. prepared nitrogen-doped porous Ti₃C₂Tₓ (N-Ti₃C₂Tₓ) by using the template of melamine-formaldehyde (MF) nanospheres. With the AC cathode, the constructed sodium ion hybrid capacitors (SICs) achieved a gravimetric energy and power density of 101.6 Wh kg⁻¹ and 3269 W kg⁻¹, respectively. Song et al. designed S-doped Ti₃C₂Tₓ aerogels (SMGA) by crosslinking S/Ti₃C₂Tₓ composites and GO sheets, with linking agents (e.g., amino-propyltriethoxysilane, Mn²⁺, Fe²⁺, Zn²⁺, and Co²⁺). The resulting electrodes exhibited excellent Na⁺ ion storage (1.26 mAh cm⁻²) with a high mass-loading (12.3 mg cm⁻²). The constructed SMGA/AC SICs displayed a capacity retention of 92.9%, and maintained a capacity of 93.7 mAh g⁻¹ (based on the anode mass) after 1600 cycles. Zhao et al. designed a 3D K⁺-pre-intercalated Ti₃C₂Tₓ MXene by alkali treatments to store K⁺ ions. The assembled 3D K⁺-Ti₃C₂Tₓ //AC potassium ion hybrid capacitors (PICs) achieved a high energy density of 163 Wh kg⁻¹ and a long-term cycling (up to 10,000 cycles), with the formation of a thin and inorganic-rich SEI in 4 m KFSI electrolytes. Owing to their fast redox kinetics, MXenes can also be used as cathodes of MIECs. For instance, Li et al. designed Sn⁴⁺ pre-intercalated Ti₂C₆ MXene (Sn⁴⁺-Ti₂C₆) cathodes with enlarged interlayer spacing for aqueous zinc ion hybrid capacitors (ZICs), with zinc metal anodes. To further shorten the diffusion length, the Sn⁴⁺-Ti₂C₆ was aligned on the carbon spheres. As expected, a specific capacity of 138 mAh g⁻¹ at 0.1 A g⁻¹ and ultralong cycling of 12,500 cycles have been achieved.

3.3. Applications in Catalysis

Recently, MXenes have attracted great attention in catalysis due to their high surface area, good electronic conductivity, and metal atom cores. Producing a large number of active catalysis sites on MXene is a widely adopted strategy to increase its performance as a catalyst, where its interactions with different metal ions are made full use of.

First, MXene-supported single metal atom catalysts (SACs@MXene) can be synthesized by anchoring metal atoms in cation vacancies or surface groups. Zhao et al. synthesized a Pt₁/Ti₃C₂Tₓ single-atom catalyst by mixing a [PtCl₆]²⁻ solution with a MXene (Ti₃C₂Tₓ) suspension, and no additional reduction operation was needed. During the process, the [PtCl₆]²⁻ ions were adsorbed on the MXene surface after mixing, and then the metal ions were self-reduced and immobilized on the Ti vacancies. By controlling
the amount of LiF used in Ti$_3$C$_2$T$_x$ MXene synthesis, the concentration of Ti vacancies could be regulated, as reported earlier. The valence state of the Pt atom was found to be between 0 and +2, with a higher oxidation state of Ti atoms. The Pt$_x$/Ti$_{1-x}$C$_2$T$_x$ had an outstanding catalytic performance for CO$_2$ functionalization, and a nearly 100% conversion rate of the CO$_2$ into CH$_3$OH in electrocatalytic CO$_2$ reduction (CO$_2$RR).[180] SACs@MXene has a high faradaic efficiency (59.1%) in molten salt etching, as mentioned earlier. The synthesized Cu MXene can also be prepared directly from MAX phases by Pd$_1$/Ti$_{3-x}$C$_2$T$_x$.[181] The valence state of the Pt atom was found to be between 0 and +2, with a higher oxidation state of Ti atoms. The synthesis of Cu SACs@MXene has a high faradaic efficiency (59.1%) in producing CH$_3$OH in electrocatalytic CO$_2$ reduction (CO$_2$RR).[180] Ramalingam et al. prepared Ru SACs@MXene by thermal annealing, after mixing a Ti$_3$C$_2$T$_x$, Ru$_x$ solution with thiourea.[181] The Ru$_x$ ions interact with the -OH terminations on the MXene surface, and are then reduced by an annealing treatment. For the hydrogen evolution reaction (HER), a low overpotential (76 mV) was achieved at a current density of 10 mA cm$^{-2}$. Second, a wide range of MXene hybrids can be synthesized by the reaction of metal salts on the MXene matrix.[124,182–186] As shown in Figure 11d, Co$_x$O$_{y}$@MXene, SnO$_2$@MXene, MnTiO$_{3-x}$@MXene, Pt@MXene, and Ag@MXene catalysts were prepared by the aerosol spray drying of MXene colloids dissolved in the corresponding metal salts, such as Co(OAc)$_2$.4H$_2$O, SnCl$_4$, Mn(CH$_3$COO)$_2$.4H$_2$O, H$_2$PtCl$_6$.6H$_2$O, or AgNO$_3$. The metal ions are distributed uniformly on the 3D MXene matrix with strong interactions, and the salt decomposes into the corresponding metal oxide or metal. Among them, Co$_x$O$_{y}$@MXene can be converted into CoP@MXene (Figure 11e) by phosphorization at high temperatures. This hybrid catalyst has a high electrocatalytic activity in the oxygen evolution reaction (OER) and the HER, with much lower overpotentials of 280 mV (10 mA cm$^{-2}$) for OER and 128 mV for HER in 1 M KOH (Figure 11f). Yu et al. fabricated FeNi-LDH/Ti$_3$C$_2$-MXene with the co-precipitation of Fe$_x$ and Ni$_x$ in a MXene dispersion,[185] during which the interaction between ions and negatively charged MXene facilitated the nucleation and anchoring of FeNi-LDH nanostructures on the MXene surface.

Recently, ordered surface-supported intermetallic compounds (IMCs, e.g., Pt$_x$Ti and Pt$_x$Nb) have been prepared using the re-active metal-support interactions on Pt/MXene catalysts. For instance, Ti$_3$C$_2$T$_x$ was first impregnated with a Pt(NH$_3$)$_4$(NO$_3$)$_2$ solution to form a fresh Pt/Ti$_3$C$_2$T$_x$ catalyst and then reduced at 550 °C in 5% H$_2$/N$_2$ for at least 0.5 h. In this process, Pt atoms are not simply embedded in the Ti$_3$C$_2$T$_x$ lattice, but form a bimetallic alloy with surfac Ti atoms, which exhibits a superior HER performance in acidic media to give a high H adsorption strength.[187,188] Pt/Nb supported on Nb$_x$CT$_x$ was prepared in a similar way, and has been reported to provide a higher H$_2$O activation than the original catalyst or pure Nb$_x$CT$_x$.[177] However, Pt atomically thin nanolayers (ATNLs) rather than Pt-Mo alloys are formed on the Mo$_x$TiC$_2$T$_x$ surface, which is explained by the preferential formation of interfacial Mo-Pt bonds and the lower interface formation energy of a Pt nanolayer than a nanoparticle.[189] The Pt ATNLs on Mo$_x$TiC$_2$T$_x$ show a stable conversion (7%) and a high selectivity (>98%) for C$_2$ products in the non-oxidative methane coupling reaction.

### 3.4. Applications in Water Treatment

Water is indispensable for life. However, the rapid development of the global economy has caused massive water pollution and waste. Investigations suggest that two million tons of sewage and other wastewater are discharged globally every day. Many water pollutants (e.g., heavy metal ions, organic chemicals, nutrient substances) have long-term negative effects on water quality and threaten human health. Therefore, water/wastewater treatment is of great importance to maintain water resources.[190] The nontoxic MXene have received growing attention due to their specific surface area and abundant surface groups, which give them and their derivatives excellent performance as adsorbents and water purification membranes.[191–197] As adsorbents, MXenes have an excellent removal efficiency and selectivity for heavy metal ions (HMI s) with the strong absorption and reducing ability.[201] Generally, the concentration of toxic HMI s (e.g., Pb$^{2+}$,[202–205] Hg$^{2+}$,[206] Ba$^{2+}$,[199,207]) in water is far lower than that of light metal ions (Li$^+$, Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$). This means that the interactions of HMI s with MXenes are strong enough to break the shielding effect of water molecules or coordinating anions, with the formation of strong bonds. As illustrated in Figure 12a, strong chemical bonds are formed between Pt and O atoms on Ti$_3$C$_2$T$_x$ due to the formation energy of Ti$_3$C$_2$(O$_2$H$_{2x_m}$Pb)$_{sy}$ being lower than that of Pb(NO$_3$)$_2$.[198] Moreover, alkali-MXene has a better efficiency for replacing F groups and metal ion (Li$^+$, Na$^+$, K$^+$) intercalation. Experimentally, a high Pb$^{2+}$ ion uptake capacity (140 mg g$^{-1}$) is achieved, with a high selectivity when other cations (e.g., Ca$^{2+}$ and Mg$^{2+}$) are also present.[208] Similarly, alkali MXene has a Ba$^{2+}$ adsorption capacity of 46.46 mg g$^{-1}$, three times that of the non-modified one.[199] It also has a ≈99% removal efficiency in a complex solution containing other elements (La, Ce, Ca, Mg, Se) contained (Figure 12b). Based on the reduction or charge transfer mechanism, some HMI s (e.g., Cu$^{2+}$,[86] Cd$^{2+}$, Cr$^{6+}$,[200] U$^{6+}$,[88]) and some oxidants (e.g., K$_3$[Fe(CN)$_6$], KMnO$_4$, Au$^{4+}$)[209] can also be removed. The residual concentration of Cr$^{6+}$ can be reduced to 5 ppb after removal by Ti$_3$C$_2$T$_x$ sheets, which meets the standard for drinking water. The removal capacity is as high as 250 mg g$^{-1}$ and is pH-dependent. In low pH or neutral solutions, Cr(VI) is reduced to Cr(III), which is anchored on the MXene surface (Figure 12c). Meanwhile, the valence state of Ti in MXene increases. The removal of Cr$^{6+}$ as cationic HCrO$_4^-$ is completed in 2 h (Figure 12d) by a RGO-intercalated Ti$_3$C$_2$T$_x$ film.[87]

As water purification membranes, Ti$_3$C$_2$T$_x$ laminates show excellent water flux and good ion sieving activity.[209] This was first reported by Ren et al., who showed that a Ti$_3$C$_2$T$_x$ film had a water flux of 37.4 L Bar$^{-1}$ h$^{-1}$ m$^{-2}$ with different ion permeation rates for Na$^+$, Li$^+$, K$^+$, Ca$^{2+}$, Ni$^{2+}$, Mg$^{2+}$ and Al$^{3+}$.[210] Given that ions permeate through the interlayer in the membranes, ions can be adsorbed on both surfaces of MXene interlayer walls, if the radius of hydrated ions are small. In this case, larger interlayer spacing can be obtained by Na$^+$ ion permutation than Ca$^{2+}$ and Al$^{3+}$ ions, as the ions with smaller hydrated radius and lower...
Figure 12. Applications of MXenes in water treatment, especially heavy metal ion removal and water purification membranes. a) Schematic of Pb^{2+} adsorption to form Ti_3C_2(O_2H^2-2mPbm). Reproduced with permission.[198] Copyright 2015, American Chemical Society. b) The removal efficiency of solute elements in simulated nuclear wastewater due to adsorption by Alk-Ti_3C_2T_x and Ti_3C_2T_x. Reproduced with permission.[199] Copyright 2018, Royal Society of Chemistry. c) Illustration of the removal mechanism of Cr(VI) from water by Ti_3C_2T_x sheets. Reproduced with permission.[200] Copyright 2015, American Chemical Society. d) Time online profiles for removal of HCrO_4^- from water. Error bars represent systematic errors in the measurements. Reproduced with permission. [89] Copyright 2019, Springer Nature. e) Schematic of Al^{3+} intercalated MXene membranes (MXMs) for effective ion sieving. The strong interaction between Al^{3+} ions and MXene layers determines the d-spacing. Hydrated cations, such as Na^+, are rejected, while the water molecules permeate the membrane. f) Time-dependent Na^+ permeation through untreated MXMs and Al^{3+}-intercalated MXMs, indicating good long-term stability of the Al^{3+}-intercalated MXMs with a much lower ion permeation rate. Na^+ permeation rates (inset) through untreated MXMs and Al^{3+}-intercalated MXMs as a function of time. Reproduced with permission. [49] Copyright 2020, Springer Nature.

3.5. Applications in Other Fields

In addition to the above applications, MXenes and MXene hybrids have been used in electromagnetic interference shielding, as sensors, and in therapeutic biomedicine. Liu et al. used the intercalation of Al^{3+} ion with additional ionic bonding to fabricate a MXene film with both flexibility and high strength.[221] The tensile strength was improved from 28.7 to 83.2 MPa, while the electronic conductivity remained at 265 600 S m^{-1}. As a result, a high EMI shielding performance (>80 dB) was obtained. MXene foams produced by Zn^{2+} crosslinking, as discussed earlier, had a shielding performance of 51.0 dB at a thickness of only 85 μm.[74] Satheeshkumar et al. used the self-reduction of specific metal ions on MXene, and synthesized Ag, Au, and Pd@MXene hybrids by one-step solution processing, as illustrated in Figure 13 a.[93] Metal nanoparticles were uniformly distributed on the surface, and a surface enhanced Raman scattering (SERS) effect was demonstrated, which can be used in sensors, catalysis, and the biomedicine. For instance, methylene blue (MB) is used as a chemical indicator, dye, biological stain, and medicine. The signal of adsorbed MB on a NP@MXene surface can be unequivocally detected in Raman spectra, even when its concentration is only 10^{-10} M (Figure 13b). Zhang et al. used the fluorescence quenching of MXene quantum dots (QDs) by Fe^{3+}, and fabricated the MXene QD fluorescent probes for specific Fe^{3+} detection.[213] The internal mechanism is based on the oxidation-reduction reaction between the MXene and Fe^{3+}, and the internal filtering effect. Similarly, Cd(II) ions in water can be pre-concentrated and self-reduced to Cd metal on Ti_3C_2T_x MXene. Then the re-oxidation signal can be measured in differential pulse voltammetry (DPV) technology,[90] and the limit of detection was low as 0.94 × 10^{-9} M.

Applications in therapeutic biomedicine are promising and may be achieved with the rational designs of MXene-based...
Figure 13. Applications of MXenes in other fields. a) Graphical representation of in-situ one-step solution processing synthesis of Ag, Au, and Pd@MXene hybrids by soft-solution processing. The inset is TEM images of MXene, Ag@MXene, Au@MXene, and Pd@MXene. b) Raman spectra of Ti$_3$C$_2$T$_x$ after soaking in MB dispersed in ethanol and subsequent drying. SERS spectra of MB with (red) Ag@, (purple) Au@, and (yellow) Pd@MXene. Reproduced with permission.[93] Copyright 2016, Springer Nature. c) Schematic of theanostic functions of MnO$_x$/Ti$_3$C$_2$-SP composites sheets, i.e., MR/PA imaging-guided efficient tumor ablation of cancer. d) In vivo PA Imaging of MnO$_x$/Ti$_3$C$_2$ nanosheets. Reproduced with permission. [214] Copyright 2017, American Chemical Society.

Dai et al. prepared MnO$_x$/Ti$_3$C$_2$ hybrids by the in situ reduction of MnO$_4^{-}$ ions on a Ti$_3$C$_2$ surface.[214] As shown in Figure 13c, the Ti$_3$C$_2$ acts as the photothermal-transducing agent for tumor ablation due to the high photothermal-conversion efficiency of MXene. MnO$_x$ acts as magnetic resonance (MR) and photoacoustic (PA) imaging contrast agents to determine tumor sites and monitor therapeutic process. In vitro and in vivo PA-imaging of MnO$_x$/Ti$_3$C$_2$ are shown in Figure 13d. Exposure to an 808 nm laser with sufficient power density, was highly efficient in causing the tumor ablation and growth suppression.

4. Summary and Prospects

This review has summarized progress on the roles of metal ions in MXene synthesis, processing and applications. Based on the way they change the MXene structure, three classifications are defined: intercalation, crosslinking, and etching. The understanding of the fundamental mechanisms has also been discussed. In the case of intercalation and crosslinking, electrostatic attraction between the metal cations and negatively charged surface groups is the driving force, and this ion exchange behavior enables the insertion of other metal ions. The hydration of metal cations plays a crucial role in improving the exfoliation kinetics and changing the interlayer spacing. Hydrated metal ions intercalate the MXene layers, rather than bare metal ions, and a large hydrated radius tends to produce a large c-LP. Metal ions with high charge tend to form strong chemical or ionic bonds with the surface groups on adjacent MXene sheets. This crosslinking by metal ions induces MXene gelation to form 3D structures, with a sufficiently high MXene concentration. In the case of etching, the charge transfer seems to be the principal reason for the formation of in-plane defects (Ti vacancies and in-plane pores), due to the redox activities of the transition metal in MXenes. In the molten salt route to synthesize MXene, Ti atoms in MAX may also be etched, similar to the Al atoms, due to the higher redox potential (M$^{2+}$/M) of MCl$_x$ salts. The energy level differences between them determine the degree of charge transfer. The quality of MXene highly depends on the choice of molten salts. In addition, the Ti vacancies can anchor reduced M atoms to form single-atom metals on MXene lattices.

The applications, by using the interactions and some targeted designs, have also been demonstrated, mainly in supercapacitors, metal-ion batteries, catalysis, and water treatment. Energy storage in MXenes is closely related to the valence of transition metal atoms. In supercapacitors with neutral electrolytes, the hydration of metal cations is thought to hinder charge transfer between intercalated cation and MXenes. As a result, only capacitive
behavior is seen. In metal-ion batteries, de-solvation and pillaring are thought to benefit ion intercalation and charge transfer. To improve the electrochemical performance, interlayer structure control, 3D structures, and MXene-based metal hybrids produced with the assistance of metal ions are used. MXene-supported single metal atom catalysts and a range of MXene metal hybrids can be prepared by the in-situ reduction or derivation of metal ions on MXenes. MXenes demonstrate excellent removal efficiency of heavy metal ions and ions sieving activities through their strong interactions with metal ions, which plays a vital role in water/wastewater treatment.

Research on interactions between metal ions and MXenes is of great importance in MXene synthesis, processing, and applications. However, there are still many issues and scientific questions to be resolved. First, research to date has mostly been focused on the Ti3C2 synthesized by the HF or LiF/HCl methods, and interactions with the same metal ions are predicted to vary with the compositions and surface terminations of MXenes. In this regard, more relevant theoretical and experimental research is urgently needed. Second, for alkali metal ions, hydration (solvation) is crucial to open the MXene interlayers but seems to hinder charge transfer, which may reduce the capacitance/capacity in energy storage. A deeper understanding of their relationships is required to explore the potential of MXenes as electrode materials. Third, the MXene crosslinking by metal ions is innovative and effective for producing 3D structure. However, relevant research is limited, and more effort is needed to regulate structural parameters, including pore size and layer thickness. Fourth, in MXene evolution from MAX phases, the kinetics of etching reactions is a crucial issue to obtain MXenes of high quality and few defects. For etching Ti3AlC2 in HF/LiCl, this is addressed by the strong bonding of Al-F and hydrated Li+ intercalation. However, the strategy of Li+ intercalation seems to play a limited role in other MXene syntheses, such as MoC2, Cr3C, or some o-MXenes (e.g., Ti2yNbyCT, V2yNbCT), which cannot be obtained in HF/LiCl. As such, there may be other important factors, and new synthesis routes for MXenes need to be investigated. Considering our current knowledge of the importance of etching and intercalation in the synthesis process, may be other ways of regulating the structure.

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Conflict of Interest

The authors declare no conflict of interest.

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[1] X. Chia, M. Pumera, Nat. Catal. 2018, 1, 909.
[2] Y. Yang, H. Hou, G. Zou, W. Shi, H. Shuai, J. Li, X. Ji, Nanoscale 2018, 11, 16.
[3] M. Zeng, Y. Xiao, J. Liu, K. Yang, L. Fu, Chem. Rev. 2018, 118, 6236.
[4] Y. Xue, Q. Zhang, W. Wang, H. Cao, Q. Yang, L. Fu, Adv. Energy Mater. 2017, 7, 1602684.
[5] C. Tan, X. Cao, X. J. Wu, Q. He, J. Yang, X. Zhang, J. Chen, W. Zhao, S. Han, G. H. Nam, M. Sindoro, H. Zhang, Chem. Rev. 2017, 117, 6225.
[6] S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Cutie’rrez, T. F. Heinz, S. S. Hong, J. Huang, A. F. ISmacht, E. Johnston-Halperin, M. Kuno, V. P. Plaschnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl, J. E. Goldberger, ACS Nano 2013, 7, 2898.
[7] M. Naguib, M. Kurtoglu, V. Presser, J. Lu, J. Niu, M. Heon, L. Hultman, Y. Gogotsi, M. W. Barsoum, Adv. Mater. 2011, 23, 4248.
[8] M. Naguib, O. Mashtalir, V. Presser, J. Lu, L. Hultman, Y. Gogotsi, M. W. Barsoum, ACS Nano 2012, 6, 1322.
[9] A. VahidMohammadi, J. Rosen, Y. Gogotsi, Science 2017, 372, 1165.
[10] M. Naguib, M. W. Barsoum, Y. Gogotsi, Adv. Mater. 2021, 33, 2103393.
[11] Y. Wei, P. Zhang, R. A. Soomro, Q. Zhu, B. Xu, Adv. Mater. 2021, 33, 2103148.
[12] Y. Li, H. Shao, Z. Lin, J. Lu, L. Liu, B. Duployer, P. O. Å. Persson, P. Ekblund, L. Hultman, M. Li, K. Chen, X.-H. Zha, S. Du, P. Rozier, Z. Chai, E. Raymundo-Piñero, P.-L. Taberna, P. Simon, Q. Huang, Nat. Mater. 2020, 19, 894.
[13] M. Li, J. Lu, K. Luo, L. Li, K. Chang, K. Chen, J. Zhou, J. Rosen, L. Hultman, P. Ekblund, P. O. Å. Persson, S. Du, Z. Chai, Z. Huang, Q. Huang, J. Am. Chem. Soc. 2019, 141, 4730.
[14] V. Kamysbayev, R. F. Klie, D. V. Talapin, A. S. F., Science 2020, 369, 979.
[15] Y. Liu, H. Xiao, W. A. Goddard, J. Am. Chem. Soc. 2016, 138, 15853.
[16] G. R. Berdiyorov, EPL 2015, 111, 67002.
[17] G. R. Berdiyorov, K. A. Mahmoud, Appl. Surf. Sci. 2017, 416, 725.
[18] I. Persson, L.-Å. Näslund, J. Halim, M. W. Barsoum, J. Palaisatis, J. Rosen, P. P. O. Å., 2D Mater. 2018, 5, 015002.
[19] X. Hui, X. Ge, R. Zhao, Z. Li, L. Yin, Adv. Funct. Mater. 2020, 30, 2005190.
[20] J. Pang, R. G. Mendes, A. Bachmatiuk, L. Zhao, H. Q. Ta, T. Gemming, H. Liu, Z. Liu, M. H. Rummeli, Chem. Soc. Rev. 2019, 48, 72.
[21] K. Li, M. Liang, H. Wang, X. Wang, Y. Huang, J. Coelho, S. Pinilla, Y. Zhang, F. Qi, V. Nicolosi, Y. Xu, Adv. Funct. Mater. 2020, 30, 2000842.
[22] M. R. Lukatskaya, O. Mashtalir, C. E. Ren, Y. Dall’Agnese, P. Rozier, P. L. Taberna, M. Naguib, P. Simon, M. W. Barsoum, Y. Gogotsi, Science 2013, 341, 1502.
[23] J. Wan, S. D. Lacey, J. Dai, W. Bao, M. S. Fuhrer, L. Hu, Chem. Soc. Rev. 2016, 45, 6742.
[24] Y. Li, Y. Lu, P. Adelhelm, M. M. Titirici, Y. S. Hu, Chem. Soc. Rev. 2019, 48, 4655.
[25] B. Anasori, M. R. Lukatskaya, Y. Gogotsi, Nat. Rev. Mater. 2017, 2, 16098.
[26] C. Zhang, Y. Ma, X. Zhang, S. Abdolhosseinizadeh, H. Sheng, W. Lan, A. Pakdel, J. Heier, F. Nüesch, Energy Environ. Mater. 2020, 3, 29.
[27] H. Chen, H. Ma, C. Li, ACS Nano 2021, 15, 15502.
[28] Y. Q. Deng, T. X. Shang, Z. T. Wu, Y. Tao, C. Luo, J. C. Liang, D. L. Han, R. Y. Lyu, C. S. Qi, W. Lv, F. Y. Kang, Q. H. Yang, Adv. Mater. 2019, 31, 1902432.
[29] Z. T. Wu, T. X. Shang, Y. Q. Deng, Y. Tao, Q. H. Yang, Adv. Sci. 2020, 7, 1903077.
[30] Y. Cui, Z. Cao, Y. Zhang, H. Chen, J. Gu, Z. Du, Y. Shi, B. Li, S. Yang, Small Sci. 2021, 1, 2100017.
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