Synthesis of MXene and its application for zinc-ion storage

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Abstract
Since 2020, some new breakthroughs in the field of MXene synthesis scheme such as water-free etching, HCl-based hydrothermal etching, halogen etching, and other novel synthesis methods have been proposed. Not only that, the application of MXene in zinc-ion storage devices has also made great progress in the past 2 years. The understanding of zinc-ion storage mechanism of MXene has undergone profound changes, and its applications have also become diversified, demonstrating the great potential of MXene for high performance zinc-ion storage devices. In this review, we have summarized the preparation and synthesis of MXene materials and systematically investigated the progress of MXene in aqueous zinc-ion storage devices. In particular, for the synthesis of MXene, we added recent reports of conventional synthesis schemes that have been widely reported to help understand their development and combined with recent novel synthesis schemes to provide a distinct partition framework. In addition, for the application of MXene, we discussed the cognitive change of zinc-ion storage mechanism of MXene and conducted an in-depth discussion about the design philosophy of MXene and their characteristics. Finally, a comprehensive perspective on the future development of MXene in the synthetic strategy and aqueous zinc-ion storage applications have been outlined.

KEYWORDS
electrochemical energy storage, MXene, MXene-based materials, zinc-ion batteries, zinc-ion capacitors

1 | INTRODUCTION

Energy is an eternal topic. The environmental pollution caused by traditional fossil fuel energy forces people to pursue new energy that is more environmentally friendly and efficient. How to store and transform energy efficiently is a huge problem. Among them, energy storage devices led by lithium-ion batteries have been commercialized after 30 years of development. However, the lack of lithium resources and the inevitable safety hazards brought by the organic system restrict its further development. Among the alternatives to lithium-ion batteries, zinc-ion storage
devices such as aqueous zinc-ion batteries (ZIBs) and zinc-ion capacitors (ZICs) have attracted much attention, not only due to the safety and nontoxicity of the aqueous system, but also due to the abundance of zinc resources and its excellent energy density and power density when used as storage electrodes.\textsuperscript{9,10} Considering that the boundary between ion batteries and ion capacitors is getting smaller and smaller, it is a more sensible decision to discuss in terms of the electrode material itself. At present, the majority cathode materials for zinc-ion storage electrode are only in the following categories, including manganese-based compounds, vanadium-based materials, and Prussian blue-based materials.\textsuperscript{9} Although manganese-based materials have relatively high capacity, due to manganese dissolution, the cycle stability of manganese oxides is generally poor.\textsuperscript{11–13} Vanadium oxides have higher capacity, but their poor electrical conductivity and fragile skeleton lead to poor cycle stability, which restricts its development.\textsuperscript{14–17} Prussian blue materials have excellent cycle stability and higher working voltage, but their capacity is generally low (50–70 mAh g\textsuperscript{-1}).\textsuperscript{18–21} For anode materials, zinc foil is often used and usually accompanied by problems such as zinc dendrites and other parasitic reactions.\textsuperscript{22,23} Therefore, there is still an urgent need to develop new and highly stable materials for high-performance zinc storage.

MXene, a general term for two-dimensional transition metal carbonitrides, carbides, and nitrides shines in the field of electrochemical energy storage due to its many unique properties. The general formula of MXene is \( \text{M}_{n+1}\text{X}_n\text{T}_x \) \((n = 1, 2, 3, 4)\), where \( \text{T}_x \) is the end-capped surface group on the outside of the transition metal M, which is introduced by etching with an etchant, and mainly includes -O, -OH, -F, or -Cl.\textsuperscript{24–31} The physical properties of MXene are superior to most two-dimensional materials. The conductivity of MXene is close to that of graphene \((10^{5–10^{6}} \text{ S m}^{-1})\); besides, the mass density is higher than that of graphene, making it have a higher energy density than that of graphene under the same mass.\textsuperscript{32–34} The mechanical properties of MXene are also excellent. With the increase of \( n \), the hardness and strength of functionalized MXene gradually increase. For the thinnest Ti\(_2\)C MXene, the strain it can withstand even exceeds that of graphene.\textsuperscript{35,36} Besides, MXene has unique electronic properties and surface chemical environment. The abundant functional groups on MXene surface make it highly hydrophilic, and it can be adjusted to switch between conductors and semiconductors. Due to the diversity of its composition and structure, MXene materials have become a large and rapidly developing two-dimensional material family.\textsuperscript{37–39} At present, more than 30 MXene materials have been synthesized, and there are more MXene materials predicted by the theory, besides the traditional ones.\textsuperscript{40,41} In addition to traditional single-metal MXene materials, two types of bimetallic MXenes including solid solution and ordered phase have been synthesized and reported.\textsuperscript{42–44} Moreover, there are also reports of MXene materials with ordered double vacancies in M\(_2\)C-type MXene materials. Due to the 33% atomic vacancies in the M layer, MXene with the general formula M\(_{1.33}\)C appears.\textsuperscript{45} The theoretical calculations of MXene predicted hundreds of possible compositions, and the formation of solid solutions at the M-position or X-position implies that an unlimited number of nonstoichiometric ratios of MXene can be synthesized.\textsuperscript{41}

At present, there have been many excellent reviews reporting the application of MXene in lithium-ion batteries,\textsuperscript{46} sodium-ion batteries,\textsuperscript{46–49} Li-S batteries,\textsuperscript{50–52} supercapacitor,\textsuperscript{53} and electrocatalysis,\textsuperscript{54} etc. These related researches have introduced the synthesis scheme of MXene and its application in different fields, which provided great guidance for its further development. The number of articles in its related fields have increased dramatically in the recent 2 years. For ZIBs, the most common Ti\(_2\)C\(_2\)T\(_x\) MXene has a very low zinc storage capacity (\(<50 \text{ mAh g}^{-1}\)) and is generally considered to be a capacitive electrode material before. The number of articles published in recent years about zinc-ion storage devices (ZIBs or ZICs) is much lower than that of the above storage devices (as shown in Figure 1A). However, the synthesis method of few classical articles on MXene has been repeatedly introduced. On the contrary, the development background of them was rarely mentioned and the similar frameworks of some reviews resulting in some inspiring articles being less quoted and unknown. Providing a different framework for the synthesis of MXene can break this mindset and help better understanding the development background of various synthesis schemes. At the same time, recent work on MXene regulation revealed that MXene actually has excellent electrochemical performance in zinc storage devices. How to regulate MXene properly and design suitable energy storage materials to help efficiently store zinc ions is a key issue of this field. It is necessary to summarize the updated research advances and provide rational guidance for their development. Obviously, we are gradually discovering that MXene has great potential and research value in the field of zinc-ion storage.

In this review, we have made a detailed classification and summary of the synthesis of MXene and discussed the regulation strategy of MXene and their applications in the field of zinc-ion storage (Figure 1B). In the first part of our review, we have reviewed the synthesis methods of MXene, including conventional wet chemical etching methods, unconventional etching schemes, and other synthesis methods, to provide a comprehensive synthesis manual of MXene for other researchers. In the second part
of our review, the storage mechanism and different regulation strategy of MXene and their applications in zinc-ion storage are reviewed. According to their design philosophy, three types of materials including pure MXene materials, MXene-based derivative materials, and MXene-based hybrid materials with their electrochemical performance of zinc-ion storage are systematically summarized, providing a good framework for their development. Finally, the challenges and problems of the synthesis methods and MXene-based materials in zinc-ion storage are pointed out, and their future development prospects are also expected.

2 | SYNTHESIS STRATEGIES OF MXENE

Most reports on MXene have the same synthetic mechanism, by using different methods to selectively remove the “A” atom in the middle layer of various A New Ternary Ceramic Material (MAX) phases. Besides, there are also some unique fabrication routes reported in recent years, such as etching of non-MAX phases and the bottom-up strategy, which use chemical vapor deposition (CVD) method to grow MXene directly. The intrinsic properties of MXene (including defects, particle sizes, and the type of
terminations on MXene and their proportion) are closely related to their synthesis strategies.

In this section, we start with the preparation of MXene, which is classified into three synthesis strategies (wet chemistry etching, unconventional etching method, and other synthetic methods), then summarize the relationship between synthesis methods and their properties by comparing their merits and demerits, as shown in Table 1. It is worth mentioning that traditional wet chemical etching methods represented by Hydrofluoric Acid (HF) and in situ formation of HF acid etching still occupy most of the reports about MXene currently.

2.1  |  Wet chemistry etching of MXene

2.1.1  |  HF etching

HF etching method, to selectively remove “A” atoms in MAX phase efficiently, is currently the most common method to synthesize MXene. It dates back to the pioneering report of Naguib et al.55 in 2011, which use 50% concentrated HF solution to selectively etch Aluminium (Al)-layer in Ti₃AlC₂ MAX phase at room temperature for 2 h. When Ti₃AlC₂ was immersed in HF, the etching reactions can be divided into two steps as following equation:

\[ \text{Ti}_3\text{AlC}_2 + 3\text{HF} = \text{AlF}_3 + 3/2\text{H}_2 + \text{Ti}_3\text{C}_2 \]  (1)

The first step is represented by reaction in Equation (1), which is essential and describes the production process of Ti₃C₂ with high surface activity. In the second step, the newly formed Ti₃C₂ will continue to react in solution and produce terminations:

\[ \text{Ti}_3\text{C}_2 + 2\text{H}_2\text{O} = \text{Ti}_3\text{C}_2(\text{OH})_2 + \text{H}_2 \]  (2)

\[ \text{Ti}_3\text{C}_2 + 2\text{HF} = \text{Ti}_3\text{C}_2\text{F}_2 + \text{H}_2 \]  (3)

But it should be noted that reactions (2) and (3) are simplified descriptions of one functional group only. The actual situation is that the terminations are combination of multiple functional groups, which depends on the etching method. The chemical formula of MXene that are etched in situ formation of HF acid etching still occupy most of the reports about MXene currently.

2.1.2  |  Fluoride-based acid etching

HF etching is currently the most widely used etching method due to its simplicity and versatility. However, due to its strong corrosiveness, high toxicity, and operational risk, researchers have to take great risks to conduct experiments. In 2014, Gogotsi and coworkers developed a relatively milder and safer in situ etching method, which used a mixed solution of fluorine salt (LiF) and other acids (HCl) to etch Ti₃AlC₂ powder and got a clay-like sediment by washing with water (Figure 2C).59

After that, other fluorine-containing salts (NaF,60 KF,61 NH₄F,62 and FeF₃63) have also been used and explored. However, it should be noted that due to the different type of positive ions introduced by different salts, the etching effect may be different. As reported by Hu et al., the solubility of different fluoride salts (LiF, NaF, and KF) and the adsorption energy of different cations (Li⁺, Na⁺, K⁺) on the surface of MXene are different. Compare with Na⁺, K⁺, the absorption energy of Li⁺ is the smallest and easiest to be adsorbed on the surface of Ti₂C. In addition, LiF is hard to dissolve in water and cannot be completely removed during cleaning, which result the atomic concentration of Li in LiF exfoliated MXene was as high as 56%, much higher than the atomic concentration of Na (3%) and K (0.1%). Due to the residual Li on surface, these kind of MXenes have different adsorption behaviors and can keep adsorbed methane.61 In 2020, Wu et al.64 discussed the etching of V₂AlC in open environment (OE) and closed environment (CE), by dissolving LiF/NaF in concentrated hydrochloric acid (HCl), followed by adding V₂AlC powders and then etching in oil bath pans (OE) or hydrothermal reaction kettles (CE). The etching environment (opened or closed) will have a decisive influence on the etching effect, NaF + HCl can be used to synthesize V₂C MXene in both CE or OE. However, LiF + HCl can be used to prepare V₂C MXene only in CE. Besides, the use of hydrochloric acid (HCl) will introduce a small amount of special -Cl groups,27 which has been confirmed and needs to be considered by researchers.
| Synthesis strategies                  | Regents                          | Morphology                                      | Merits                                      | Demerits                                      |
|---------------------------------------|----------------------------------|------------------------------------------------|---------------------------------------------|-----------------------------------------------|
| HF etching                            | HF                               | Accordion-like structure with abundant -F      | 1. Effective for most MAX                   | 1. Dangerous operation                        |
|                                       |                                  | terminations and defects                       | 2. High yield                               | 2. Cannot be peeled in situ                   |
| Fluoride-based acid etching           | LiF/NaF/KF + HCl NH₄HF₂          | Clay-like MXene with large interlayer spacing and few -F terminations | 1. Relatively safe                          | 1. Long etching time                          |
|                                       |                                  |                                                | 2. Direct ultrasonic peeling                | 2. Introducing fluoride salt impurities       |
| Alkaline solution etching             | NaOH TMAOH                       | Accordion-like structure only with -O₂, -OH terminations (For TMAOH terminated with Al(OH)₄⁻) | 1. No risk of acid corrosion                | 1. For NaOH: severe etching conditions        |
|                                       |                                  |                                                | 2. Fluorine-free functional group           | 2. For TMAOH: need HF pretreatment            |
| Molten fluoride salt and Lewis acidic molten melts etching | LiF+NaF+KF Lewis Acid | Accordion-like structure (For Lewis Acid terminated with various halogens) | 1. For molten fluoride salt: can obtain nitride MXene | 1. Introduce salt impurities                  |
|                                       |                                  |                                                | 2. For Lewis acid: achieve precise control of surface functional groups | 2. Severe etching conditions                  |
| Electrochemical etching               | NH₄Cl+TMAOH                      | Single or few-lawyer structure without -F      | 1. Safe etching environment                 | 1. Strict etching conditions                  |
|                                       |                                  | functional group                               | 2. Fluorine-free functional group           | 2. Introduce salt impurities                  |
|                                       |                                  |                                                | 3. Get stripped MXene directly             |                                               |
| Water-free etching                    | NH₄HF₂ in organic solvents       | Accordion-like structure with extremely high -F terminations | 1. Conductive to the use of organic systems due to the absence of water | 1. Long etching time                          |
|                                       |                                  |                                                | 2. Can be delaminated directly by ultrasonication | 2. Tedious washing steps                      |
| HCl-based hydrothermal etching        | HCl-hydrothermal                 | Layered structure with -Cl and -O terminations | 1. Simple experiment operation             | 1. Severe etching conditions                  |
|                                       |                                  |                                                | 2. Fluorine-free functional group           | 2. Rely on the prediction of precise reaction conditions by DFT |
| Halogen etching                       | Br₂, I₂, ICl, IBr                | Accordion-like structure terminated with various halogens | 1. Mild etching environment                | 1. Tedious etching and purification steps     |
|                                       |                                  |                                                | 2. Precise control of surface functional groups | 2. Strict etching condition                   |
| Chemical vapour deposition (CVD)      | Methane and bimetal foil (Cu/Mo) | Ultra-thin and large-size flake                | 1. High purity                             | 1. Low productivity                          |
| process                               |                                  |                                                | 2. Accurate control of thickness            | 2. High synthesis temperature                |
| Lithiation-expansion-microexplosion mechanism | Lithium-ion | Single-layer or few-layer structure without -F functional group | 1. Simple and safe synthesis environment    | 1. Low productivity                          |
|                                       |                                  |                                                | 2. Fluorine-free functional group           | 2. Consume resources                         |
| In Situ electrochemical synthesis     | LiTFSI + Zn(OTF)₂                | In situ etching and stripping in the battery   | 1. Green synthetic environment friendly     | 1. Rely on expensive metal ion salts          |
|                                       |                                  |                                                | 2. Extremely convenient operation           | 2. Restricted to be used inside the battery   |

Abbreviation: DFT, density functional theory; TMAOH, TetraMethyl Ammonium Hydroxide.
Ammonium bifluoride also proved to be an effective means of etching Ti$_3$AlC$_2$. In 2017, Feng and coworkers reported a special NH$_4$HF$_2$ etchant, which can selectively etch the Al atoms in Ti$_3$AlC$_2$. The obtained Ti$_3$C$_2$ MXene has a larger interlayer spacing due to the insertion of NH$_4^+$, and its lattice parameter $c$ was up to 24.9 Å. In addition, NH$_4^+$ adsorbed on the surface of Ti$_3$C$_2$ can hinder the oxidation reaction between O$_2$ and Ti$_3$C$_2$, and NH$_4^+$ can also absorb heat and then become volatile NH$_3$. These two effects together enhance the thermal stability of Ti$_3$C$_2$.

2.2 Unconventional etching method of MXene

2.2.1 Alkaline solution etching

The successful use of acid etching can naturally make people think of whether alkali can be used to etch MAX. Theoretically, because HF or in situ generated HF is dangerous and harmful to the environment, the use of alkali etching can effectively solve this problem. At the same time, the use of alkali etching can remove the -F surface functional groups at the source of the etching, which is considered to be unfavorable for energy storage.

From the perspective of the stability constant of the complex, the alkali solution can theoretically etch Ti$_3$AlC$_2$, but in fact the etching reaction is difficult to occur, which may be due to the oxide layer (Al$_2$O$_3$) formed on the surface of Al layer. It has been found that strong alkali (NaOH) or organic alkali (TMAOH) can be used to etch Ti$_3$AlC$_2$. There have been many reviews introducing these two types of work, but it should be noted that some of them have incorrect causality. They claim that due to strong alkali etching requires high temperature and high pressure hydrothermal environment, which has high safety risks, thus a safer organic alkali etching has been developed. In fact, the organic alkali etching scheme was reported in
2016, and the mature strong alkali etching scheme was only proposed in 2018, these two schemes do not have the above causal relationship.

Geng et al. reported the use of TMAOH to successfully etch Ti$_3$AlC$_2$. First, a low concentration of HF is used to pretreat Ti$_3$AlC$_2$ for a short time to remove the surface oxide, and then TMAOH is used as an etchant to react to obtain Ti$_2$C$_2$ with Al(OH)$_4$ as terminals. And the TMA$^+$ inserted between the layers can expand the layer spacing. Interestingly, TMAOH is usually used as an intercalant to produce single-layer or multi-layer MXene by intercalation and ultrasonic, and reports of its use as an etchant are very rare.

The use of organic alkali etching still requires the use of dangerous HF for pretreatment, which actually poses a safety hazard to the operator. In addition, the concentration of HF pretreatment needs to be carefully adjusted to ensure that it only partially removes the oxide layer on the surface of Ti$_3$AlC$_2$ and does not completely etch the MAX phase. The above multistep operations increase the complexity of its operation. Inspired by the Bayer process for refining bauxite in the aluminum industry, Li et al. conducted a series of explorations of hydrothermal temperature and NaOH concentration and found that under the conditions of 270$^\circ$C and 27.5 M NaOH, the obtained MXene has the highest purity of 92%. Li’s work pioneered the use of high-temperature and high-concentration alkali etching. The high temperature guarantees the transformation of the primary product (Al(OH)$_3$ and AlO(OH)) into the dissolvable Al(OH)$_4^−$ so that the etching reaction continues to occur, and the high NaOH concentration can ensure the purity of MXene by avoiding the formation of NTO like Na$_2$Ti$_3$O$_7$ or Na$_2$Ti$_5$O$_{11}$ (Figure 3A).

2.2.2 | Molten fluoride salt and Lewis acidic molten melts etching

There are many differences between carbide MXene and nitride MXene. The cohesive energy of nitride MXene is lower than that of carbide MXene, so its stability is lower and may lead to dissolution in HF. In addition, the formation energy of nitride MXene from the precursor is higher, which makes the M-Al bond energy stronger and requires much higher energy to remove Al atoms. In 2016, Urbankowski et al. proposed a short period and effective etching method, by using a molten fluorine-containing salt mixture of LiF, NaF, and KF as an etchant to obtain the first two-dimensional transition metal nitride MXene (Figure 3B). Although the X-ray diffraction (XRD) pattern shows that the obtained MXene has low crystallinity compared to carbide MXene, this etching scheme using high-temperature melt etching opens up a new way of synthesizing MXene.

In addition to melting fluorine-containing salt, Lewis acid molten salt has also been proved to be an effective means to etch the MAX phase. The “A” atom in the MAX precursor and the cation in the Lewis acid are removed by oxidation-reduction reaction. Using the relationship between their electrochemical oxidation-reduction potentials in the halide melt can guide the selection of effective Lewis acids for a variety of untraditional MAX precursors. In 2020, Talapin et al. proposed a general strategy and synthesized a variety of MXenes with a single surface terminations (O, S, Se, Cl, Br, NH, and Te) as well as bare MXene without surface termination (Figure 3C) and found that some of the Nb$_2$C series MXenes, including Nb$_2$C$_x$ MXene, have superconductivity under low temperature conditions. Recently, the Lewis acid molten salt method has produced MXene with unitary, binary, and ternary halogen terminals for use in zinc ion batteries. All in all, the use of Lewis acid molten salt to etch MXene can significantly control the surface state and structure of MXene, thereby having a decisive impact on the performance of MXene. At present, there is still relatively little related work, and more exploration in this direction is needed in the future.

2.2.3 | Electrochemical etching

The essence of chemical etching is that the “A” atoms in the MAX phase transfer electrons, thereby driving the occurrence of electrochemical reactions. Based on this, Yang and coworkers innovatively proposed an electrochemical etching method for a two-electrode system, using NH$_4$Cl and TMAOH (TetraMethyl Ammonium Hydroxide) to configure a weakly alkaline solution with PH > 9 as the electrolyte and successfully prepared a small layer and large lateral size Ti$_3$C$_2$T$_x$ (T = OH, O) MXene. However, the toxicity of the intercalant may cause safety problems in the laboratory. In 2019, Pang et al. proposed a thermally assisted electrochemical etching scheme, using porous carbon fiber cloth as a substrate and highly conductive carbon black (CB) as an additive, a 3D composite electrode was constructed, and dilute hydrochloric acid was used as an etchant to accelerate the etching in a mildly heated environment to prepare Ti$_x$C$_2$T$_x$ MXene (Figure 3D). And the mild electrochemical etching strategy was extended to synthesize V$_2$C$_x$T$_x$ and Cr$_2$C$_x$T$_x$ MXene, which are more difficult to manufacture by conventional etching schemes.

Electrochemical etching is an effective etching method to prepare fluorine-free MXene. However, the design of the electrolyte, the control of the reaction time, and the selection of the etching voltage all have a crucial influence on
FIGURE 3  (A) Schematic of the reaction between Ti$_3$AlC$_2$ and alkaline solution under different conditions. Reproduced with permission. Copyright 2018, Wiley-VCH. (B) Schematic illustration of the synthesis of Ti$_3$N$_x$T$_y$ MXene by molten salt treatment. Reproduced with permission. Copyright 2016, Royal Society of Chemistry. (C) Schematic of the surface reactions of MXenes in molten inorganic salts. Reproduced with permission. Copyright 2020, the authors, published by American Association for the Advanced of Science. (D) Schematic illustration of the electrochemical etching mechanism of Ti$_2$AlC in HCl electrolyte. Reproduced with permission. Copyright 2019, American Chemical Society. (E) Schematic of water free etching by organic solvents and NH$_4$HF$_2$. Reproduced with permission. Copyright 2020, Elsevier. (F) Schematic illustration of the preparation of fluoride-free Mo$_2$CT$_x$ by sole HCl-assisted hydrothermal etching strategy. Reproduced with permission. Copyright 2021, Wiley-VCH. (G) Schematic of halogen etch of MAX phases. Reproduced with permission. Copyright 2021, American Chemical Society.
the successful synthesis of MXene, which is undoubtedly a huge challenge for its wider promotion.

2.2.4 | Water-free etching

At present, most etching schemes, whether electrochemical etching method or acid or alkali solution etching, use water as the solvent. However, the presence of water may hinder the occurrence of certain specific reactions, and the prepared MXene must go through vacuum annealing to avoid the presence of trace water that may have a huge impact on the performance of organic system such as sodium-ion batteries.

Recently, Michel W. Barsoum’s group proposed a scheme to etch Ti3AlC2 with organic solvents, by using a variety of organic solvents (propylene carbonate [PC], N, N- dimethylformamide, dimethyl sulfoxide, etc.) and ammonium bifluoride (NH4HF2) (Figure 3E); the MAX phase is etched to get a significantly increased interlayer spacing and a super high fraction of -F termination (≈70%) MXene.75 In addition, the Ti3C2Tx synthesized using PC solvent has nearly doubled its capacity when applied to sodium-ion batteries compared to those etched in water, which shows the powerful potential of this method. However, at present, the use of organic solvents to synthesize MXene requires a long etching time (196 h). Besides, it needs to be operated in a glove box to ensure an anhydrous environment, and multi-step washing operations are required to remove byproducts and residual acidic propanol detergents, which brings great inconvenience to the operation of the experimenter.

2.2.5 | HCl-based hydrothermal etching

Under normal conditions, only HF can effectively etch the “A” element in the MAX phase. However, in principle, additional energy can be applied to form soluble AlCl3 or GaCl3 to complete the etching process.

Inspired by this, Wang et al.76 used first-principle to calculate the feasibility of using hydrochloric acid-assisted hydrothermal to etch Al or Ga at different temperatures and pressures. Then based on the guidance of density functional theory (DFT) results, the MAX phases such as Mo2Ga2C were successfully etched, and Mo2CTx MXene with only -O and -Cl terminations was obtained (Figure 3F). It is worth mentioning that compared with the Mo2CTx MXene obtained by hydrofluoric acid etching, the fluoride-free MXene obtained by hydrochloric acid hydrothermal shows a different capacitance behavior.

Etching strategies based on the feasibility of DFT simulation and optimal reaction conditions can significantly improve the efficiency of traditional exploration by trial-and-error etching experiments, which provides a new idea for the etching of MAX phase.

2.2.6 | Halogen etching

In the early days, halogen was used to extract synthetic carbon materials from Ti3SiC2 MAX. Ti3SiC2 was chlorinated with Cl2 in a quartz tube furnace for 3 h to extract titanium and silicon from it to obtain nanoporous carbide-derived carbon.77

Recently, Shi et al.78 proposed a method to synthesize MXene with iodine etching in anhydrous acetonitrile (CH3CN) and remove the reaction product AlI3 with hydrochloric acid to obtain a medium-sized, high-oxygen-content layered MXene. The solution is simple and convenient but still requires a higher reaction temperature (100°C). Besides, Vaia et al.79 proposed a scheme to use halogen (Br2, I2, ICl, and IBr) etching of Ti3AlC2 to synthesize halogen-terminated MXene (Figure 3G). Compared with the Lewis acid molten salt method that requires high temperature conditions, the conditions of this scheme are milder and safer, and it can be synthesized at room temperature using a glove box. It is worth mentioning that the experimenters optimized all the experimental procedures involving the use of halogens. For example, the stabilizer tetrabutylammonium bromide was added to stabilize the corrosion byproducts and ensure the safety of the process. More importantly, the free radical mechanism proposed by the researchers may be the key to halogen etching of MXene. For the reaction of Br2, Br2 is adsorbed on the exposed edge of the Al plane and is homogenized. The generated free radicals react with the Al center and the solvent. Then the author speculates that the high-temperature molten salt etching of MXene may have a similar mechanism to this scheme, that is, in situ production of halogen radicals.

The halogen etching method not only provides more solutions for controlling the surface chemistry to modulate the properties of MXene but also allows us to have a deeper understanding of the etching mechanism of MXene.

2.3 | Other synthetic methods of MXene

2.3.1 | CVD process

All etching schemes are based on the precursor to selectively remove the “A” atomic layer to obtain MXene. The lateral dimension of the chemically derived MXene is between several hundreds of nanometers to ~10 μm. In 2015, Xu et al.80 proposed a bottom-up synthesis strat-
FIGURE 4  (A) Schematic illustration of the growth of Mo$_2$C crystals under low and high flow rates of CH$_4$. Reproduced with permission. Copyright 2017, Wiley-VCH. (B) Schematic of the Ti$_3$C$_2$T$_x$ MXene prepared by lithiation intercalation-expansion-microexplosion process. Reproduced with permission. Copyright 2019, American Chemical Society. (C) Schematic illustration of the in situ electrochemical etching mechanism. Reproduced with permission. Copyright 2020, Wiley-VCH.

... Using CVD to directly synthesize ultra-thin (several nanometers thick) and large-size (over 100 microns) α-Mo$_2$C crystals. The carbon source is methane, and the molybdenum source is the molybdenum foil under the copper foil (these two foils constitute a bimetal foil). Cu melts and Mo atoms diffuse to the surface and react with the carbon atoms generated by the decomposition of methane when the temperature is above 1085°C, so as to directly synthesize Mo$_2$C crystal. Two years later, the lateral dimensions of Mo$_2$C synthesized by the CVD method reached the centimeter level (Figure 4A).81

The CVD method can be used to control the synthesis of MXene, and the obtained MXene has large lateral dimensions, uniform thickness, and low defect concentration. However, the control process parameters are complicated, including the duration, reaction temperature, and gas (methane). In 2020, Goknur Cambaz Buke’s group systematically studied the influence of impurities in the system, the thickness of the copper substrate, and the formation of graphene on the copper surface before Mo$_2$C formation on the morphology and thickness of Mo$_2$C crystals, which is of great significance for its synthesis guidance.82

2.3.2 Lithiation–expansion–microexplosion mechanism

There have been several reports on the synthesis of fluorine-free MXene, but there are still some technical difficulties in using simple and controllable solutions...
to directly obtain high-purity single-layer or few-layer MXene.

Recently, Sun and collaborators developed a new method of preparing single-layer or few-layer MXene.\(^{83}\) At the first stage, Ti\(_3\)AlC\(_2\) raw material was used as anode, and lithium foil was the cathode and reference electrode. After the discharge process at 0.10 mA, lithium-ion intercalation was used to form Al-Li alloy, which expands in volume. After ultrasonic treatment in distilled water, Li\(_x\)Al\(_y\) will have a microexplosion reaction and etch out ultra-thin Ti\(_3\)C\(_2\)T\(_x\) MXene (Figure 4B). In addition, silicon-based MAX Ti\(_3\)SiC\(_2\) is also used to synthesize MXene, which proves the universality of the method.

2.3.3 | situ electrochemical synthesis

The traditional method of synthesizing MXene requires etching and then device assembly, which is a multistep protocol and is not environmentally friendly. Recently, Zhi's group proposed an integrated process that combines the situ etching of MAX and ions storage of MXene.\(^{84}\) By using LiTFSI and Zn(OTF)\(_2\)-mixed ionic electrolyte as the etchant, V\(_2\)CT\(_x\) MXene is synthesized through an electrochemical process inside the battery (Figure 4C). It is worth noting that during the lifetime of the battery, the device has experienced exfoliation, oxidation of the electrode material, and redox reaction of the oxidation product V\(_2\)O\(_3\). The resulting ZIB provides a capacity of 409.7 mAh g\(^{-1}\) at 0.5A g\(^{-1}\), and an energy density as high as 310.3 Wh kg\(^{-1}\). This MAX-devices-derived MXene-devices solution is quite inspiring, creating a precedent for green and convenient production of MXene devices.

3 | MXENEBASED MATERIALS FOR ZINCION STORAGE APPLICATIONS

3.1 | The zinc storage mechanism and design philosophy of MXene

Although many synthetic schemes for MXene have been reported, the traditional wet chemical etching scheme is simpler and more efficient than the unconventional etching method of MXene and other special synthetic methods. As a result, HF etching and fluoride-based acid etching method still account for the majority of MXene reports in zinc-ion storage devices, which may cause the relationship between MXene synthesis and performance to be ignored.

One of the most appropriate examples of the relationship between MXene synthesis and performance is the discussion of the storage mechanism of MXene. Different synthetic schemes may result in different zinc-ion storage behavior of MXene, which will help us better understand the storage mechanism of MXene in zinc-ions batteries. MXene has been considered to rely on the adsorption and desorption mechanism on the material surface for zinc-ion storage for several years. The pure MXene material synthesized by traditional HF etching method exhibits low reversible capacity in ZIBs, which can be confirmed from the cyclic voltammogram (CV) curve. Generally speaking, in the aqueous electrolyte, the CV of MXene mainly shows a rectangle without obvious redox peaks,\(^{72}\) which is different from the performance in organic electrolytes, implying that the pure MXene material absorbs zinc-ions to complete ion storage in a double-layer capacitor mode, or is accompanied by a certain surface pseudocapacitance reaction.\(^{85}\) Besides, Song and coworkers designed carbon nanotube (CNT) delaminated V\(_2\)C MXene (DV\(_2\)C@CNT) and applied it to a ZIC and discovered the co-intercalation behavior of zinc-ions and hydrogen-ions during cycling.\(^{86}\) However, due to the choice of new synthesis schemes, the understanding of zinc-ion storage mechanism of MXene has undergone profound changes. Recently, the Lewis acidic molten melts etching method was used in MXene zinc-ion storage devices, and a new storage mechanism was developed, which expanded the understanding of MXene storage mechanism. In the early 2021, Huang et al.\(^{72}\) used Lewis acid molten salt etching method to synthesize MXene with unit, binary, and ternary halogen functional groups. Part of the halogen-terminated MXene has a characteristic redox peak observed in cyclic voltammetry, and multi-halogen-terminated MXene has double redox peaks, which is quite different from the conventional hydrofluoric acid etching effect (to produce MXene with oxygen and fluorine terminals). This work reveals the different reaction mechanisms caused by the difference of MXene surface functional groups. The electrochemical activities of -Br and -I endow the reversible redox reaction that MXene covered by traditional Oxygen and Fluorine (OF) functional groups does not have, resulting in a new halogenation conversion reaction of zinc-ion storage mechanism. It is worth mentioning that the synthetic strategy of MAX-devices derived MXene-devices in ZIBs has also been discovered by the same research group.\(^{87}\) In the future, the relationship between the synthesis of MXene and the electrochemical performance of zinc-ion energy storage devices needs further discussion.

In addition to the synthesis method, the test conditions were also found to be related to the storage mechanism of MXene in zinc-ions storage devices. Recently, Li et al.\(^{88}\) found that when broaden the scan voltage up to 2.4 V, a distinct potential plateau of Nb\(_2\)CT\(_x\)/Zn battery was achieved, the higher voltage activates different active storage sites of zinc-ions, which gave the battery storage features of pure MXene in aqueous ZIB system and realized the zinc-ion
### Table 2
Summary the design philosophy, regulation ideas corresponding methods, and corresponding characteristics of MXene

| Design philosophy | Regulation ideas | Methods | Characteristics |
|------------------|------------------|---------|-----------------|
| Pure MXene materials | 1. Layer spacing control  
2. Surface functional group control  
3. Special structure design | 1. Electrolyte additives  
2. In situ spontaneously reducing/assembling  
3. Vacuum filtration  
4. Intercalation of ions or small molecules  
5. In situ surface growth vertical arrangement | 1. Diversified applications  
2. Low capacity as cathode material  
3. Diversification of regulation |
| MXene-based derivative materials | 1. Partly regulated oxidation  
2. In situ oxidation phase transition  
3. Spontaneous phase transitions | 1. Hydrothermal process  
2. One-step annealing approach  
3. In situ electrochemical activation  
4. In situ electrolyte oxidation | 1. Simple and convenient experiment  
2. High capacity due to derivatives  
3. Fast ion diffusion ability due to the retention of MXene 2D structure  
4. Restrained by the choice of limited precursors |
| MXene-based hybrid structure | 1. With manganese-based oxide: MnO₂, MnOₓ, ZMO  
2. With vanadium-based oxide: V₂O₅·nH₂O, H₂V₃O₈, NHVO  
3. With TMDs or LDH | 1. Gas-phase spray  
2. Liquid phase mixing stirring or/and filtrating  
3. Facile hydrothermal reaction  
4. Electrostatic self-assembly strategy | 1. Longer experimental period  
2. Hybrid materials alleviate MXene stacking problems and provide capacity  
3. MXene acts as a conductive skeleton to keep the structure stable and realize the rapid transport of electrons and ions |

intercalation and de-intercalation mechanism. There is no doubt that the cognition of zinc-ion storage mechanism is constantly changing and developing. In-depth exploration of the zinc-ion storage mechanism of MXene is of great significance for its rational design guidance.

The applications of pure MXene materials in zinc-ion storage devices are diverse, and rational design is the key to realize their efficient applications. On the other hand, in addition to regulating pure MXene to become a suitable anode or cathode material for zinc-ion storage, MXene also has the characteristics of easy oxidation or other phase transitions, thus gradually developed a strategy of in situ oxidation based on V₂C MXene to construct a zinc-ion storage cathode material. Finally, MXene has good hydrophilicity, excellent conductivity, and stable structure, which is considered to be the starting material to build a hybrid structure with active materials to construct cathode or anode materials.

In the following sections, we focus on the current research work on MXene-based materials for zinc-ion storage (including ZIBs and ZICs). According to the design philosophy of MXene summarized above, its specific application can be divided into three categories: pure MXene materials for zinc storage, MXene-based derivative materials for zinc storage, and MXene-based hybrid structure for zinc storage. We systematically summarize the design philosophy and regulation strategies with main characteristics of MXene materials applied to zinc storage, and provide certain guidance for its development (Table 2).

### 3.2 Pure MXene materials for zinc storage

#### 3.2.1 Design philosophy

Two-dimensional layered compounds are considered to be able to store ions effectively. As a new type of two-dimensional material, MXene has been discussed in many theoretical calculations and experimental work for storing various types of ions. However, due to the different storage mechanism of zinc-ions in MXene, pure MXene materials synthesized under conventional conditions are rarely reported in cathode materials. Generally, the capacity of the synthesized pure MXene material itself as the cathode material for ZIB is much lower than that of other cathode materials, and the capacity can be improved by adjusting the structure of the layer spacing or special structural designing to meet the rapid diffusion of zinc-ions. Besides, a more suitable choice is to use it as the cathode or
anode material of ZIC to realize high capacitance of zinc-ion adsorption/desorption storage by using its huge surface accumulation, or adjust the anode electrode of zinc foil for ZIB by using MXene as zinc-ion nucleation inducer or electrolyte additive.

3.2.2 Cathode for zinc-ion storage

The two-dimensional MXene material produced by etching has an obvious defect. Due to the presence of its surface functional groups, the surface activity increases, which is prone to stacking and restricts the transmission of ions. DFT shows that increasing the MXene layer spacing can significantly increase the capacity, thanks to larger storage space and stable multilayer adsorption. The use of ions, small molecules, or polymer intercalation MXene to expand the interlayer spacing has been proven to be an effective way to alleviate the stacking problem and increase the storage capacity of alkali metal ions. The use of Ti3C2 for zinc-ion hybrid capacitor, for the first time using cationic surfactant (CTAB) to dissolve in ZnSO4 electrolyte, and CTAB was spontaneously embedded in the MXene to achieve in situ column support, which stabilizes the structure of Ti3C2 and expands the layer spacing. As an electrode material, the obtained MXene has excellent cycle stability, and the cycle capacity retention rate reaches 96% after 1000 cycles; for the first time it has been confirmed that zinc ions can be reversibly stored in layered MXene. In addition, the 1D core-shell structure of bacterial cellulose (BC)@polypyrrole (PPy) nanosfibers is also used to expand the interlayer spacing of MXene. The embedded nanofibers have excellent conductivity and provide additional capacity. The resulting hybrid electrode exhibits an excellent performance of 388 mF cm⁻², which is much higher than pure MXene material without structure adjustment.

However, the expansion of the interlayer spacing can only facilitate ion diffusion, but it cannot shorten the ion transmission path. Based on this, Zhi and coworkers recently proposed a unique in situ growth of the vertical arrangement of MXene synthetic method. By mixing Ti powders, Al powders, carbon sphere, and other molten salts and then heating them in a tube furnace, the MAX phase successfully grew on the surface of the carbon balls and synthesized the core–shell structure Ti2AlC/C spheres vertically arranged on the surface. Then, the obtained Ti2AlC/C spheres were etched by HF for 10 h and then dissolved in the SnCl4 solution. After 24 h treatment, Sn⁴⁺ spontaneously intercalated between the layers, and the interlayer spacing was expanded from 1.15 nm to 1.27 nm, successfully fabricating the Sn⁴⁺-Ti2CT/C sphere with enlarged interlayer spacing and vertical arrangement structure (Figure 5A). Compared with the random distribution of Ti2CT/C particles, the vertically arranged structure caters to the transmission direction of different ions, thus shortening the transmission path. At the same time, the pillar effect generated by the insertion of Sn⁴⁺ ions is used to increase the ions storage space and improve the shuttle kinetics of ions. Besides, Scanning Electron Microscope (SEM) (Scanning Electron Microscope) results confirm that 2D MXene flakes are arranged orderly and vertically and on the outer surface of the carbon sphere (Figure 5B). As the cathode material of ZICs, Ti2CT/C supported by Sn⁴⁺ pillars with a vertical arrangement structure (Sn⁴⁺-Ti2CT/C) exhibits excellent cycle life (12 500 cycles under 0.5 A g⁻¹) and low self-discharge performance (0.989 mV h⁻¹) (Figure 5C). Besides, in 2019, Zhi’s group applied the pure MXene material to zinc storage for the first time, by preparing stripped Ti2CT MXene nanosheets, and then vacuum filtration to obtain a flexible MXene film, which was used as a cathode material for ZICs and a collection of anode materials’ fluid. Using the feature that Ti3C2 can be oxidized by medical H2O2 into harmless TiO2 nanoparticles, a full-component degradable zinc ion capacitor is prepared. After seven days of degradation in the phosphate buffer saline solution and the next few hours of medical H2O2 assistance, the assembled ZIC achieved full-component degradation (Figure 5D). SEM images reveal that the thickness of the zinc nanosheets anchored on the self-supporting MXene film is only 30–50 nm, forming a 3D porous structure to increase the specific surface area, which is beneficial to its corrosion degradation (Figure 5E,F).

3.2.3 Anode for zinc-ion storage

In addition to being used as a cathode material, MXene is also considered to be an excellent anode material in ZICs. The capacitive electrode material of the traditional ion capacitor electrode generally uses activated carbon, but activated carbon can only use the double-layer energy storage mechanism to absorb and store ions, which reduces the energy density of the system and causes the problem of capacitance mismatch. Based on this, Wang et al. proposed a new design method, using MnO2-based materials (MnO2–CNTs) as the battery-type cathode material, and MXene as the capacitive anode material. The energy storage mechanism of MXene’s insertion and extraction is used to eliminate the mismatch problem in kinetics and capacitance. Recently, Zeng and coworkers used δ-MnO2@carbon cloth battery-type cathode and MXene@cotton cloth capacitor-type anode assembled into flexible asymmetric storage device (Figure 5G). The SEM image shows that the layer MXene nanosheets grow on cot-
FIGURE 5  (A–C) Schematic illustration of synthetic process, SEM image, and anti-self-discharge performance of core-shell Sn4+-Ti2CTx/C sphere. Reproduced with permission. Copyright 2020, Wiley-VCH. (D–F) Digital images of the degradation of the whole solid-state Zn-MXene capacitor, top-view SEM images, and cross-section SEM images of metallic Zn electrodeposited onto Ti3C2 film. Reproduced with permission. Copyright 2019, American Chemical Society. (G–I) Schematic diagram, SEM image, and electrochemical performance of δ-MnO2@CAC//MXene@COC. Reproduced with permission. Copyright 2019, Elsevier. (J–N) Schematic diagram of MXene self-assembly on Zn surface, SEM image, elemental mapping images of MXene-coated Zn, electrochemical performance of symmetric cells, and Zn/MnO2 batteries with pure Zn and MZn-x. Reproduced with permission. Copyright 2020, Wiley-VCH
ton cloth exhibiting the smooth surface (Figure 5H). As a new flexible ZIC, the δ-MnO₂@C@C//MXene@COC system device exhibits both high energy density (90 Wh kg⁻¹) and high power density (3838 W kg⁻¹), with high capacitance retention of 80.7% after 16 000 cycles (Figure 5I). In addition to manganese oxide, vanadium oxide is also used as cathode material to assemble zinc-ion storage devices with 2D MXene as the capacitive anode material. Gao et al. demonstrated a zinc-ion hybrid micro-supercapacitor (ZIHMSC) by designing vanadium oxide (V₂O₅)-based electrode as battery-type cathode and Ti₃C₂Tₓ MXene-based electrode as capacitor-type anode. The obtained flexible ZIHMSC exhibits a remarkable capacitance (129 mF cm⁻² under 0.34 mA cm⁻²) and well-cycle stability (retaining 77% capacitance after 10 000 cycles).¹⁰¹

The zinc anode electrode of aqueous ZIBs is often accompanied by serious dendrites problems. Apart from directly making ZIC anode materials, MXene has also been developed in the application of inhibiting zinc dendrites. In 2020, Niu and coworkers first proposed a synchronously reducing and self-assembling process to grow MXene on the surface of the zinc anode (Figure 5J).¹⁰² Top view SEM results indicate that the in situ grown MXene layer is uniformly anchored on the surface of the Zn foil (Figure 5K,L). Compared with the accidental manual operation, the interface layer produced by in situ growth is more uniform and stable, which smooth the Zn deposition on anode surface. The electrochemical performance test was carried out in a symmetrical cell, and the zinc anode assembled after 60 min (MZn-60) has a stable voltage curve, displaying a small voltage with a lower voltage fluctuations hysteresis of 47 mV for 400 cycles (Figure 5M). In addition, when using conventional manganese dioxide as the cathode to assemble a full battery, thanks to the suppression of zinc dendrites, the MZn-60/MnO₂ battery shows a high initial capacity (252.8 mAh g⁻¹) and long cycle stability with a retention rate of 81% at 1 A g⁻¹ (Figure 5N). In addition to the above strategy by using MXene as electrolyte additive to form buffer layer on zinc anode surface, in situ growth of MXene protective layer on zinc anode surface¹⁰³ and using Sb-modified MXene paper to construct alloying-type zinc storage materials¹⁰⁴ to avoid the formation of zinc dendrites are also proposed. Recently, Zhi’s group used MXene as the inorganic filler of the solid electrolyte and chemically grafted the surface of MXene with poly(methyl acrylate) to increase its compatibility with the polymer, and then uniformly dispersed it in polyvinylidene fluoride-co-hexafluoropropylene (PVHF) to prepare a solid polymer electrolyte PVHF/MXene-g-PMA.¹⁰⁵ The assembled solid full cells suppresses the zinc dendrites and other side reactions and maintains excellent stability in high and low temperature environments. There is no doubt that as a new type of two-dimensional material, MXene’s application range in zinc-ion storage is constantly being explored.

3.2.4 Summary

According to the above examples, regarding the structure and surface regulation, we summarize several common applications of pure MXene in zinc storage. Unlike organic systems, in which MXene is generally only used as the negative electrode material, MXene has a diversified application in zinc storage and can be divided into the following categories: (1) zinc-ion storage cathode material for ZIB, (2) anode or cathode material for ZIC, (3) Zn foil anode protective layer, and (4) as an electrolyte additive. The excellent electrical conductivity, abundant surface functional groups, and stable 2D structure of MXene itself are the keys to its multiple applications in zinc storage. In addition, it is worth noting that the storage capacity of the pure MXene material is very low when used in ZIBs. The source of this problem may be related to its storage mechanism and requires more exploration and research in the future.

3.3 MXene-based derivative materials for zinc storage

3.3.1 Design philosophy

Although there have been many reports on MXene materials used in lithium-ion batteries and sodium-ion batteries, there are few reports on the pure MXene materials in ZIBs, for the reason that MXene materials exhibit unreasonable low discharge capacity in ZIBs. The possible reason is that the surface transition metal of MXene material has a low average valence state, and it is impossible to achieve multi-electron redox reaction through the conversion of high and low valence states during the storage of zinc-ions.¹⁰⁶ Vanadium oxides such as V₂O₅ have high discharge capacity due to the multi-electron oxidation-reduction reaction of vanadium, and a variety of vanadium oxide-based materials have been used as cathode materials for aqueous ZIBs. V₂C MXene material has excellent electrical conductivity and rich surface chemistry, and its accordion structure can facilitate ion transmission to improve the diffusion ability of electrode materials. If V₂C MXene is derived into vanadium oxide and retains its unique accordion-like conductive V-C-V two-dimensional layered structure, theoretically, MXene-based materials with high stability and rapid zinc-ion migration can be realized, which exhibits the great structural advantages of MXene-based derived materials and solves the problem of poor conductivity and unstable structure of traditional V₂O₅ materials. Based on the above
3.3.2 Cathode for zinc-ion storage

Chou and coworkers achieved in situ electrochemical activation of V\textsubscript{2}C materials by initial charging at different potential (1.4 V, 1.8 V, 2.0 V) (Figure 6A).\textsuperscript{106} The activated electrode material inherits the accordion shape of V\textsubscript{2}C MXene, which is conducive to the rapid migration and storage of zinc-ions (Figure 6B). In addition, after the surface of the material is sputtered by Ar ion, X-ray photoelectron spectroscopy (XPS) results show that as the etching depth increases, the peak intensity of low-valence V gradually increases, which proves that the oxidation of the V-valence state only occurs on the surface of V\textsubscript{2}CT\textsubscript{x}. As the electrode of ZIB, the obtained electrochemical activation MXene cathode exhibits a high capacity of 423.5 mAh g\textsuperscript{-1} at 1 A g\textsuperscript{-1}. It is worth noting that the discharge capacity of 1.8-V\textsubscript{2}C is almost unaffected as the current density increases (the discharge capacity remain to be 398.1, 386, 378, 371, 365, and 358 mAh g\textsuperscript{-1} when at 5, 10, 15, 20, 25, and 30 A g\textsuperscript{-1}), the rate performance is almost a straight line (Figure 6C).

On the basis of the above in situ electrochemical approach, a series of other easy and effective methods
about preparing derived materials of $V_2C$ MXene have been proposed recently. Yan et al.\textsuperscript{107} used a simple hydrothermal process to synthesize $V_2O_5@V_2C$ nanohybrid structure through oxidation of V-MXene at various temperatures (Figure 6D). Field Emission Scanning Electron Microscope (FESEM) on the microstructure reveals that the crystalline $V_2O_3$ nanorods can grow on the external surface with the existence of stacked $V_2C$ layers at the appropriate temperature (Figure 6E). The $V_2O_5@V_2C$ nanohybrid cathode delivers a high reversible capacity of 397 mAh g\(^{-1}\) at 0.5 A g\(^{-1}\) and 290 mAh g\(^{-1}\) at 4 A g\(^{-1}\) (Figure 6F). The higher discharge capacity and superior rate capability can be ascribed to the improvement of electron and ion mass transfer rate for the oxygen vacancy and defect carbon of the surface electronic structure of $V_2O_3$. In addition to the above method, Feng’s group reported a one-step annealing approach to synthesize the microsized $V_2O_5$ arrays with nanoporous structure.\textsuperscript{108} During the anneal process, the $V_2CT_x$ sheets start to granulate and thicken, gradually oxidized to $V_2O_5$. As the cathode for ZIBs with hydrogel electrolyte, the derived $V_2O_5$ shows excellent electrochemical performance (250.4 mAh g\(^{-1}\) at 8000 mA g\(^{-1}\)).

In addition to the above methods, Li et al.\textsuperscript{109} demonstrate a zinc hybrid-ion battery (ZHIB) that $V_2C$ MXene cathode can stratify and undergo unexpected phase transitions during the cycle to generate $V_2O_5$, making the capacity continue to rise even within 18 000 cycles (Figure 6G). After 18 000 cycles, the surface morphology of $V_2CT_x$ changed significantly, its smooth surface became rough, and dense granular products were formed (Figure 6H). Combine ex situ XRD, XPS, and High Resolution Transmission Electron Microscopy (HRTEM) images, which proved the occurrence of phase transition and the generation of $V_2O_5$. As a ZHIB electrode, the obtained MXene derivative materials show high energy density (386.2 Wh kg\(^{-1}\) at 0.2 A g\(^{-1}\)) and remarkable ultralong cycle performance (up to 18 000 cycles at 10 A g\(^{-1}\)) (Figure 6I). It is worth mentioning that this result is more superior than almost all aqueous ZIBs, representing a supercompetitive electrochemical performance. Besides, Zhi’s group reported that the fluorine-rich electrolyte can be used as the etchant to in situ electrochemically synthesize MXene-based ZIBs.\textsuperscript{84} During the electrochemical reaction, the MAX phase $V_2AlC$ was completely etched to $V_2CT_x$ MXene by F-contained electrolyte at first stage, and the $V_2CT_x$ MXene is oxidized to be $V_2O_5$ in the second stage (Figure 6J). After multiple cycles, the internal carbon layers connect the oxidized $V_2O_3$ forming a sandwich like $V_2O_5/C/V_2O_5$ structure, which is beneficial to overall conductivity and improves zinc ion transportation. HRTEM result confirms the uniform distribution of $V_2O_5$ particles on the 2D carbon layers (Figure 6K).

As a result, the $V_2AlC$-devices-derived $V_2C$-devices deliver high energy density (33 Wh kg\(^{-1}\) when achieving the highest power density of 17 192.5 W kg\(^{-1}\)), which surpasses most reported V-based cathodes (Figure 6L). It is worth mentioning that the oxidation process of $V_2C$ during the electrochemical cycle has also been reported in ZnSO\(_4\) electrolyte, implying the instability of $V_2C$ in aqueous systems.\textsuperscript{33}

3.3.3 | Summary

Based on the examples mentioned above, the derivative MXene materials can be obtained by several synthetic methods, including assembling the battery and subsequent in situ electrochemical activation, and assembling zinc-ion energy storage device and subsequent in situ electrolyte oxidation, hydrothermal process, and one-step annealing approach. At present, the main method uses $V_2C$ to derive $V_2O_5$ to provide an ideal solution to the problem of low capacity of pure MXene materials. These unique MXene-based derivative materials have the following advantages: (1) simple and convenient experiment; (2) high capacity due to derivatives; (3) fast ion diffusion ability due to the retention of MXene 2D structure, which becomes the remarkable electrode material with high capacity, high rate performance, and capacity retention ability by selecting the appropriate MXene precursor and rationally regulating the structure of the derivative product. Unfortunately, this in situ derivation strategy is restrained by the choice of limited precursors. In fact, it has been confirmed that $V_2C$ MXene is oxidized at high potential to produce a new oxidation product phase. However, it is still uncertain whether this mechanism of using phase transition to store zinc-ions is equally effective for other MXenes. The fundamental reason may be the different electronegativity and different number of electrons in the d orbital of different elements, resulting in different MXene with distinct properties. Being more familiar with the properties of the elements in the periodic table may better guide us to find suitable MXene precursors and predict possible electrochemical behavior.

3.4 | MXene-based hybrid structure for zinc storage

3.4.1 | Design philosophy

MXene is considered to be ideal substrate material due to the high conductivity and adjustable surface chemical properties for combining with other substances. Not only that, its density is higher than that of tradi-
tional two-dimensional carbon materials such as graphene (∼4 g cm⁻³), so it has a higher volumetric energy density, and is often used to composite with high-capacity active materials. Among them, the active material is the main contributor to the capacity, and the MXene substrate provides a stable load structure, which prevents the agglomeration of active materials to slow down the volume expansion, and facilitates the transmission and diffusion of electrons. At present, there have been many reports on the application of MXene and active nanomaterials to organic system such as Lithium-ion Batteries (LIBs) and Sodium-ion Batteries (SIBs). The related development has become mature, and its application in ZIBs is still in its early stages. Therefore, in this section, several examples of common hybrid structures will be introduced, and reasonable development ideas will be provided.

3.4.2 | Cathode for zinc-ion storage

In 2019, Luo et al.¹¹⁰ used a simple solution stirring method to prepare manganese oxide (MnO₂) and layered MXene (Ti₃C₂Tx) composite hybrid material (Figure 7A) and fabricated the freestanding electrode by filtering the mixture of composite materials and continuous CNTs. After functionalizing by potassium permanganate (KMnO₄), manganese oxide (MnO₂) will both decorated onto the MXene surface and bond to the innerside of each MXene flakes (Figure 7B). Thanks to the interpenetrating nanoscale conductive components composed of active materials and CNTs, the zinc-ion electrode material maintains an energy density of about 50% at a high power density of 10 000 W kg⁻¹ (Figure 7C), which demonstrates the excellent rate performance of MnO₂@Ti₃C₂Tx and shows application potential for rapid charging and discharging. In addition to the most common Ti₃C₂Tx MXene, V₂C MXene is also used as base to construct nano-hybrid material. Recently, Zhu et al.¹¹¹ synthesized the manganese–vanadium hybrid material (K–V₂C@MnO₂) by facile hydrothermal reaction (Figure 7D). After alkalization-treated by KOH, K-V₂C presents a more obvious layered structure due to the expansion of the interlayer spacing after the intercalation of K⁺ ions (Figure 7E,F). In addition, the potassium ions adsorbed on the surface is able to act as the template to form MnO₂ with K-birnessite structure. Multilayered V₂C MXene in the hybrid structure not only promotes the conductivity of the active material and inhibits the MnO₂ from aggregation during repeated charge–discharge process but also enables rapid electron and Zn²⁺ ion transport. In turn, MnO₂ nanosheets in the nanocomposites acting as active material increase the deposition area for promoting electrochemical utilization. Therefore, the obtained K–V₂C@MnO₂ exhibits outstanding long-term cycling stability due to the excellent structure stability and rapid ion transport dynamics (Figure 7G).

The above scheme mainly uses layered MXene as the composite substrate. Recently, Shi and coworkers proposed a facile gas-phase spray drying approach to synthesize a MXene@MnO₂ hybrid material with 3D microflower structure (Figure 7H).¹¹² SEM result shows that the synthesized 3D microflower has a size of about 2.5 microns and a rough surface with numerous ridges (Figure 7I). Additionally, at a high current density of 500 mA g⁻¹, the hybrid electrode can retain a capacity about 92.7% after 800 charging–discharging cycles and 90.6% after 2000 cycles, which is much better than various MnO₂-based cathodes in aqueous ZIBs (Figure 7J). Besides, Feng’s group used S-doped MXene@MnO₂ as the cathode material and assembled it with Zn@3D Ti–TiO₂ anode to form a full battery.¹¹³ This battery system has excellent cycle stability, the capacity remains 95.46% even after 500 cycles at the current density of 5A g⁻¹.

Additionally, the combination of spinel-type materials and MXene has also been proved to be an effective method for constructing durable and flexible aqueous ZIBs. Peng et al.¹¹⁴ used a facile one-part synthetic hydrothermal method to prepare spinel ZnMn₂O₄ (ZMO) and Ti₃C₂Tx hybrid nanoparticles (Figure 7M). Characterization on the microstructure reveals that the obtained 3D MXene interpenetrating assembly ZMO@Ti₃C₂Tx has a large number of ZMO nanoparticles anchored on the surface (Figure 7N). Then the zinc anode, active material cathode, and gel electrolyte are used to assemble flexible aqueous ZIBs. The assembled device shows high mechanical stability, and the discharge curves almost overlap

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**Figure 7** (A–C) Schematic illustration of the synthesis, SEM image, and electrochemical performances of MnO₂@Ti₃C₂Tx. Reproduced with permission.¹¹⁰ Copyright 2019, Wiley-VCH. (D–G) Schematic diagram, SEM image, elemental mapping images, and electrochemical performances of K–V₂C@MnO₂. Reproduced with permission.¹¹¹ Copyright 2021, American Chemical Society. (H–L) Schematic diagram, SEM image, and electrochemical performances of 3D Ti₃C₂Tx@MnO₂ microflowers. Reproduced with permission.¹¹² Copyright 2020, Royal Society of Chemistry. (M–O) Schematic illustration, SEM image, and electrochemical performances at various deformation states of ZMO@Ti₃C₂Tx. Reproduced with permission.¹¹³ Copyright 2020, Elsevier. (P–R) Schematic diagram, Transmission Electron Microscopy (TEM) image, and electrochemical performances of H₂V₃O₈/MXene. Reproduced with permission.¹¹⁴ Copyright 2020, Elsevier
under bending and twisting, which reveals the robust electrochemical performance of flexible ZIBs under different deformations (Figure 7O).

Other than manganese oxide and zinc manganese oxide, combining MXene with vanadium oxide and layered double hydroxide (LDH) can also construct MXene-based hybrid structure. Liu et al. [115] designed a H$_2$V$_3$O$_8$ nanowire (NW)/MXene composite material through a simple hydrothermal reaction strategy (Figure 7P). H$_2$V$_3$O$_8$ NWs are directly grown on the surface of MXene (Figure 7Q); the uniform distribution of Ti and V elements under the FESEM image proves the good combination of vanadium oxide and MXene. Thanks to the excellent conductivity of the hybrid structure and ion transport kinetics, the composite material exhibits a larger capacity and longer cycle stability and delivers capacities of 73 mAh g$^{-1}$ for over 500 cycles even at 20 A g$^{-1}$ (Figure 7R). Similarly, Xu and his coworkers used a simple one-step hydrothermal method to synthesize a unique V$_2$O$_x$nH$_2$O/MXene composite exhibiting a high specific capacity (over 300 mAh g$^{-1}$ at 0.1A g$^{-1}$). [116] In addition, the electrostatic self-assembly strategy based on MXene has also been used to construct high-performance cathode materials for aqueous ZIBs. Zhang et al. successfully synthesized the 2D/2D co-doped NiMn-LDH/V$_2$CTx MXene (CNMV) electrode materials by electrostatic self-assembly of co-doped LDH and V$_2$CTx MXene. Acting as the cathode for ZIBs, CNMV exhibits a considerable energy density of 368.7 Wh kg$^{-1}$ at a power density of 246 W kg$^{-1}$.[117]

3.4.3 Anode for zinc-ion storage

Generally speaking, the regulation of anode electrode materials of ZIBs mainly focuses on the regulation of zinc anode. Such strategies cannot fundamentally solve the problem of zinc dendrite. In recent years, a few metal-free anode materials with low redox potential have been explored. In 2021, Wang et al. [118] first mixed (NH$_4$)$_2$V$_{10}$O$_{25}$·8H$_2$O (NHVO) nanobelts with MXene nanosheet solution and successfully prepared NHVO@Ti$_3$C$_2$Tx hybrid film through vacuum filtration. The prepared anode film material exhibits an impressive capacity of 514.7 mAh·g$^{-1}$ at 0.1 A g$^{-1}$, further proving the huge application potential of vanadium oxide and MXene composite material as anode material for aqueous ZIBs. As proof of concept, a “rocking chair” zinc-ion full battery was constructed in combination with ZnMn$_2$O$_4$ cathode, showing an energy density of 97.1 Wh kg$^{-1}$. Recently, Zeng et al. [119] synthesized MXene-TiS$_2$ (de)intercalation anode material through ultrasonic strategy and combined with vanadium oxide and gel electrolyte to build a flexible self-healable zinc-ion microbattery, further expanding the application of MXene hybrid material in the anode electrode for ZIBs.

3.4.4 Summary

According to description of the above examples, MXene-based hybrid structures can be obtained by the following methods, including liquid phase mixing stirring or/and filtrating, facile hydrothermal reaction, gas-phase spray, and electrostatic self-assembly strategy. MXene-based hybrid materials have a wide range of applications and can be used as high-performance cathode or anode electrode materials. When used as a high-performance electrode material, the design of a hybrid structure requires the compounding of MXene and the active substance compared with in situ derivation, which is accompanied by a longer experimental period. In the hybrid structure, the self-stacking problem of MXene has been alleviated, thanks to the introduction of hybrid materials. In addition, the layered or exfoliated MXene acts as a conductive substrate; its excellent conductivity, stable mechanical properties, and abundant surface functional groups are easy to recombine, making it an excellent carrier for active nanomaterials and a skeleton that facilitates the rapid migration of ions and electrons. It is worth noting that when used as an electrode material for ZIBs, apart from the only one report on the composite with transition metal sulfide TiS$_2$, most of MXene related work is composited with vanadium oxide-based and manganese oxide-based materials, which virtually limits its development. In addition, considering that the composite potential and working voltage of MXene and different materials will have a large difference, when conducting battery performance testing, researchers should consider in advance whether the prepared material is suitable as an anode material or a cathode material.

4 CONCLUSIONS AND PERSPECTIVES

This review summarized the synthesis of MXene and its basis in zinc-ion storage devices in terms of their regulation, properties, and performance. The characteristics, advantages, and disadvantages of various synthesis schemes are carried out in the first part. Later, the most current advances about the storage mechanism and three different kinds of design philosophy for zinc-ion storage of MXenes are presented in the second part.

Generally speaking, MXene has made new breakthroughs in the field of synthesis in recent 2 years. Based on this, we first systematically summarize the synthesis scheme of MXene, especially including the new progress in recent 2 years, and provide a different division framework
from most previous reports. We try to introduce the synthesis schemes of various MXene in detail, by describing its development background rather than just introduced the specific experimental scheme, so that readers can understand its development context more clearly. In addition to the storage application of MXene, after several years of development, MXene has made great progress in common organic system energy storage devices such as lithium-ion batteries and sodium-ion batteries. However, the development of MXene in aqueous zinc-ion storage devices including ZIBs and ZICs is still in its infancy, which just began since the third quarter of 2019. Based on this, we have described the storage mechanism of zinc-ions in MXene and summarized the current reports on the application of MXene for zinc-ion storage, and provide a framework for its development in zinc-ion storage devices. According to the different design philosophy and modification ideas of MXene, its application in zinc-ion storage can be divided into: (a) pure MXene materials for zinc Storage; (b) MXene-based derivative materials for zinc storage; and (c) MXene-based hybrid structure for zinc storage. Because of its capacitive storage mechanism under usual conditions, pure MXene material is directly applied to the cathode material of ZIBs with low capacity, so that it is often used in capacitors as an adsorption type anode or cathode material, or the regulating material of zinc anode electrode of ZIB. In addition, by regulating the oxidation of MXene properly to synthesize MXene derivatives-MXene hetero-junction structure, the retention of the two-dimensional structure of MXene will facilitate the rapid migration of zinc-ions, and the derivative products on the surface will be the main contribution to the capacity. Moreover, the excellent electrical conductivity and mechanical stability of MXene itself will serve as a substrate to prevent the structural damage of the derivative product during the cycle, so that its cycle stability is significantly improved.

### Table 3: Summary of design philosophy of MXene and their electrochemical performance for zinc-ion storage applications

| Design philosophy | Electrode material | Electrolyte | Electrochemical performance | Refs |
|-------------------|--------------------|-------------|-----------------------------|------|
| Pure MXene materials | CTAB ex situ pillared Ti$_3$C$_2$ | 0.1 M ZnSO$_4$ | 52 mAh g$^{-1}$ at 0.2 A g$^{-1}$ | 95 |
| | Sn$^{4+}$.Ti$_3$C$_2$/C | 21 M LiTFSI + 1 M Zn(OTf)$_2$ | 138 mAh g$^{-1}$ at 0.1 A g$^{-1}$ | 97 |
| | Ti$_3$C$_2$I$_2$ | 21 M LiTFSI + 7 M LiOTf + 1 M Zn(OTf)$_2$ | 135 mAh g$^{-1}$ at 0.5 A g$^{-1}$ | 72 |
| | DV$_2$C@CNT | 1 M ZnSO$_4$ | 190 F g$^{-1}$ at 0.5 A g$^{-1}$ | 86 |
| | Ti$_3$C$_2$/Zn@Ti$_3$C$_2$ | 1 M ZnSO$_4$ | 330 F cm$^{-2}$ (132 F g$^{-1}$) at 0.5 A g$^{-1}$ | 98 |
| | MnO$_2$–CNTs/Ti$_3$C$_2$ | 2 M ZnSO$_4$ + 0.1 M MnSO$_4$ | 115 F g$^{-1}$ at 1 mV s$^{-1}$ | 99 |
| | $\delta$-MnO$_2$@CAC //MXene@COC | 2 M ZnSO$_4$ + 0.1 M MnSO$_4$ | 126 F g$^{-1}$ at 1 mV s$^{-1}$ | 100 |
| | V$_2$O$_3$/MXene | 2 M ZnSO$_4$ | 129 mF cm$^{-2}$ at 0.34 mA cm$^{-2}$ | 101 |
| | CNTs@MnO$_2$ //MXene/BC@PPy | 2 M Zn(CF$_3$SO$_3$)$_2$ + 0.1 M MnSO$_4$ | 290 F cm$^{-2}$ at 0.75 mA cm$^{-2}$ | 96 |
| MXene-based derivative materials | VO$_x$.V$_2$CT$_x$ | 3 M ZnSO$_4$ + 1 M Li$_2$SO$_4$ | 423.5 mAh g$^{-1}$ at 1 A g$^{-1}$ | 106 |
| | V$_2$O$_5$@V$_2$CT$_x$ | 1 M ZnSO$_4$ | 107 mAh g$^{-1}$ at 1 A g$^{-1}$ | 33 |
| | V$_2$O$_5$@V$_2$C | 2.5 M ZnSO$_4$ | 397 mAh g$^{-1}$ at 0.5 A g$^{-1}$ | 107 |
| | V$_2$O$_5$ | 2 M Zn(OTf)$_2$ | 358.7 mAh g$^{-1}$ at 0.2 A g$^{-1}$ after 400 cycles | 108 |
| | V$_2$O$_5$/C/V$_2$O$_5$ | 21 M LiTFSI + 1 M Zn(OTf)$_2$ | 409.7 mAh g$^{-1}$ at 0.5 A g$^{-1}$ | 84 |
| | V$_2$CT$_x$/V$_2$O$_5$/C | 21 M LiTFSI + 1 M Zn(OTf)$_2$ | 508 mAh g$^{-1}$ at 0.2 A g$^{-1}$ | 109 |
| MXene-based hybrid structure | 3D Ti$_3$C$_2$T$_x$@MnO$_2$ | 2 M ZnSO$_4$ + 0.1 M MnSO$_4$ | 301.2 mAh g$^{-1}$ at 0.1 A g$^{-1}$ | 112 |
| | MnO$_2$@Ti$_3$C$_2$ | 2 M ZnSO$_4$ + 0.2 M MnSO$_4$ | 88 mAh g$^{-1}$ at 0.1 A g$^{-1}$ | 110 |
| | K–V$_2$C@MnO$_2$ | 2 M ZnSO$_4$ + 0.25 M MnSO$_4$ | 408.1 mAh g$^{-1}$ at 0.3 A g$^{-1}$ | 111 |
| | ZMO@Ti$_3$C$_2$ | 1 M ZnSO$_4$ + 0.05 M MnSO$_4$ | 172.6 mAh g$^{-1}$ at 0.1 A g$^{-1}$ | 113 |
| | V$_2$O$_5$–nH$_2$O/Ti$_3$C$_2$ | 3 M Zn (CF$_3$SO$_3$)$_2$ | 323 mAh g$^{-1}$ at 0.1 A g$^{-1}$ | 116 |
| | H$_2$V$_2$O$_5$/MXene | 3 M Zn (CF$_3$SO$_3$)$_2$ | 365 mAh g$^{-1}$ at 0.2 A g$^{-1}$ | 115 |
| | LDH/V$_2$CT$_x$ | 2 M ZnSO$_4$ + 0.2 M MnSO$_4$ | 322.7 mAh g$^{-1}$ at 0.2 A g$^{-1}$ | 117 |
| | NHVO@Ti$_3$C$_2$ | 3 M Zn (CF$_3$SO$_3$)$_2$ | 514.7 mAh g$^{-1}$ at 0.1 A g$^{-1}$ | 118 |
| | MWCNTs-VO$_2$ (B)//MXene-Ti$_3$S$_2$ | ZnSO$_4$-PAM hydrogel | 40.8 mAh cm$^{-2}$ at 0.29 mA cm$^{-2}$ | 119 |
mechanism. Besides, it can have a variety of different morphologies according to the choice of synthesis scheme, but it usually requires a more complicated synthesis route and a longer synthesis cycle. The electrochemical performance of MXene in zinc-ion storage applications under three different design philosophy are summarized in Table 3.

MXene has excellent hydrophilicity, outstanding electrical conductivity close to graphene, and remarkable mechanical properties. Not only that, its rich and adjustable functional groups on the surface result in realizing different physical and chemical properties. The adjustable properties of MXene is its most important feature compared to other two-dimensional materials (such as graphene, which also have excellent electrical conductivity). However, there are many problems and challenges need to be overcome. Based on this, several suggestions are put forward to promote the synthesis methods and the application of MXene in zinc-ion storage devices:

1. More other options for etching schemes should be tried; at present, there have been different types of MXene synthesis schemes, considering the high efficiency and universality, the current mainstream synthesis scheme of MXene is still the most common HF etching and fluorine-containing salt etching, which may limit the development and application of MXene. There is no doubt that the various types of MXene obtained through multiple synthesis schemes will expand our understanding of its electrochemical energy storage applications.
2. MXene synthesis scheme with more consideration of safety and low cost method; although the cost of MAX phase have been greatly reduced in recent years, its further synthetic MXene scheme still lacks the value of practical application. There is still a certain distance from the age when MXene is comparable to graphene.
3. More synthesis method and theoretical calculation should be taken, to give a better understanding of the zinc-ion storing mechanism for MXene and a rational explanation for its low capacity problem.
4. More materials should be selected and explored; in addition to the typical Ti-based MXene Ti3C2 and V-based MXene V2C, more other types of MXene need to be explored and applied to diversify MXene. Besides, other than manganese oxide and vanadium oxide, the choice of other active materials combined with MXene material needs to be considered.
5. Taking into account the safety and nontoxic characteristics of zinc-ion storage devices, which are suitable for daily production. Therefore, more consideration should be given to the preparation of MXene-based flexible electrode materials and the development of nontoxic and degradable MXene materials, so as to find more opportunities to realize valid and practical zinc-ion storage devices.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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REFERENCES

1. Dunn B, Kamath H, Tarascon JM. Electrical energy storage for the grid: a battery of choices. Science. 2011;334(6058):928-935.
2. Soloveichik GL. Battery technologies for large-scale stationary energy storage. Annu Rev Chem Biomol Eng. 2011;2(1):503-527.
3. Goodenough JB. Changing outlook for rechargeable batteries. ACS Catal. 2017;7(2):1132-1135.
4. Kim TH, Park JS, Chang SK, Choi S, Ryu JH, Song HK. The current move of lithium ion batteries towards the next phase. Adv Energy Mater. 2012;2(7):860-872.
5. Su S, Ma J, Zhao L, et al. Progress and perspective of the cathode/electrolyte interface construction in all-solid-state lithium batteries. Carbon Energy. 2021;3(6):866-894.
6. Liu B, Jia Y, Li J, et al. Safety issues caused by internal short circuits in lithium-ion batteries. J Mater Chem A. 2018;6(43):21475-21484.
7. Liu J, Hu J, Deng Q, et al. Aqueous rechargeable batteries for large-scale energy storage. Isr J Chem. 2015;55(5):521-536.
8. Zhao Y, Yuan X, Jiang L, et al. Regeneration and reutilization of cathode materials from spent lithium-ion batteries. Chem Eng J. 2020;383:123089.
9. Jia X, Liu C, Neale Z, Yang J, Cao G. Active materials for aqueous zinc ion batteries: synthesis, crystal structure, morphology, and electrochemistry. Chem Soc Rev. 2020;120(15):7795-7866.
10. Zhang N, Chen X, Yu M, Niu Z, Cheng F, Chen J. Materials chemistry for rechargeable zinc-ion batteries. Chem Soc Rev. 2020;49(13):4203-4219.
11. Fang G, Zhu C, Chen M, et al. Suppressing manganese dissolution in potassium manganate with rich oxygen defects engaged high-energy-density and durable aqueous zinc-ion battery. Adv Funct Mater. 2019;29(15):1808375.
CHEN et al.

12. Han M, Qin L, Liu Z, et al. Reaction mechanisms and optimization strategies of manganese-based materials for aqueous zinc batteries. *Mater Today Energy*. 2021;20:100626.

13. Gao X, Zhang H, Liu X, Lu X. Flexible Zn-ion batteries based on manganese oxides: progress and prospect. *Carbon Energy*. 2020;2(3):387-407.

14. Liu C, Neale Z, Zheng J, et al. Expanded hydrated vanadate for high-performance aqueous zinc-ion batteries. *Energy Environ. Sci.* 2019;12(7):2273-2285.

15. Qian L, Wei T, Ma K, Yang G, Wang C. Boosting the cyclic stability of aqueous zinc-ion battery based on Al-doped V2O5·12H2O cathode materials. *ACS Appl Mater Interfaces*. 2019;11(23):20888-20894.

16. Chen H, Huang J, Tian S, et al. Interlayer modification of pseudocapacitive vanadium oxide and Zn(H2O)n+2 migration regulation for ultrahigh rate and durable aqueous zinc-ion batteries. *Adv. Sci.* 2021;8(14):2004924.

17. Wang P, Shi X, Wu Z, Guo S, Zhou J, Liang S. Layered hydrated vanadium oxide as highly reversible intercalation cathode for aqueous Zn-ion batteries. *Carbon Energy*. 2020;2(2):294-301.

18. Chae MS, Heo JW, Kwak HH, Lee H, Hong ST. Organic electrolyte-based rechargeable zinc-ion batteries using potassium nickel hexacyanoferrate as a cathode material. *J Power Sources*. 2017;337:204-211.

19. Paolella A, Faure C, Timoshovskii V, et al. A review on hexacyanoferrate-based materials for energy storage and smart windows: challenges and perspectives. *J Mater Chem A*. 2017;5(36):18919-18932.

20. Wang B, Han Y, Wang X, et al. Prussian blue analogs for rechargeable batteries. *Science*. 2018;363:110-113.

21. Liu Y, Huang M, Xiong F, Zuo J, An Q. Improved zinc-ion storage performance of the metal-free organic anode by the effect of binder. *Chem Eng J*. 2022;482:131092.

22. Li X, Li Q, Hou Y, et al. Toward a practical Zn powder anode: Ti3C2Tx MXene as a lattice-match electrons/ions redistributor. *ACS Nano*. 2021;15(9):14631-14642.

23. Du W, Ang EH, Yang Y, Zhang Y, Ye M, Li CC. Challenges in the material and structural design of zinc anode towards high-performance aqueous zinc-ion batteries. *Energy Environ. Sci.* 2020;13(10):3330-3360.

24. Deysher G, Shuck CE, Hantanasirisakul K, et al. Synthesis of Mo9VA1C4 MAX phase and two-dimensional Mo1.33C1.33 MXene with five atomic layers of transition metals. *ACS Nano*. 2020;14(1):204-217.

25. Halim J, Cook KM, Naguib M, et al. X-ray photoelectron spectroscopy of select multi-layered transition metal carbides (MXenes). *Appl Surf Sci*. 2016;362:406-417.

26. Hope MA, Forse AC, Griffith KJ, et al. NMR reveals the surface functionalisation of Ti3C2Tx MXene. *Phys Chem Chem Phys*. 2016;18(7):5099-5102.

27. Kajiyama S, Szabova L, Linuma H, et al. Enhanced Li-ion accessibility in MXene titanium carbide by steric chloride termination. *Adv Energy Mater*. 2017;7(9):1601873.

28. Soundiraraju B, George BK. Two-dimensional titanium nitride (Ti,N) MXene: synthesis, characterization, and potential application as surface-enhanced raman scattering substrate. *ACS Nano*. 2017;11(9):8892-8900.

29. VahidMohammadi A, Rosen J, Gogotsi Y. The world of two-dimensional carbides and nitrides (MXenes). *Science*. 2021;372(6547):1581.

30. Du C-F, Sun X, Yu H, et al. V4C3Tx MXene: a promising active substrate for reactive surface modification and the enhanced electrocatalytic oxygen evolution activity. *Infomat*. 2020;2(5):950-959.

31. Yi J, Li J, Huang S, et al. Ti3CTx MXene-based all-optical modulator. *Infomat*. 2019;2(3):601-609.

32. Anasori B, Lukatskaya MR, Gogotsi Y. 2D metal carbides and nitrides (MXenes) for energy storage. *Nat Rev Mater*. 2017;2(2):16098.

33. Venkatkarthick R, Rodthongkum N, Zhang X, et al. Vanadium-based oxide on two-dimensional vanadium carbide MXene (V2O5@V2CTx) as cathode for rechargeable aqueous zinc-ion batteries. *ACS Appl Energy Mater*. 2020;3(5):4677-4689.

34. Zhang J, Kong N, Uzun S, et al. Scalable manufacturing of freestanding, strong Ti3C2Tx MXene films with outstanding conductivity. *Adv Mater*. 2020;32(23):200193.

35. Borysiuk VN, Mochalin VN, Gogotsi Y. Molecular dynamic study of the mechanical properties of two-dimensional titanium carbides Ti6+nCn (MXenes). *Nanotechnology*. 2015;26(26):265705.

36. Guo Z, Zhou J, Si C, Sun Z. Flexible two-dimensional Ti6+nCn (n = 1, 2 and 3) and their functionalized MXenes predicted by density functional theories. *Phys Chem Chem Phys*. 2015;17(23):15348-15354.

37. Kamysbayev V, Filatov AS, Hu HC, et al. Covalent surface modifications and superconductivity of two-dimensional metal carbide MXenes. *Science*. 2020;369(6506):979-983.

38. Khazaei M, Ranjbar A, Arazi M, Sasaki T, Yunoki S. Electronic properties and applications of MXenes: a theoretical review. *J Mater Chem C*. 2017;5(10):2488-2503.

39. Liu Y, Xiao H, Goddard WA. Schottky-barrier-free contacts with two-dimensional semiconductors by surface-engineered MXenes. *J Am Chem Soc*. 2016;138(49):15853-15856.

40. Gogotsi Y, Anasori B. The rise of MXenes. *ACS Nano*. 2019;13(8):8491-8494.

41. Tan TL, Jin HM, Sullivan MB, Anasori B, Gogotsi Y. High-throughput survey of ordering configurations in MXene alloys across compositions and temperatures. *ACS Nano*. 2017;11(5):4407-4418.

42. Anasori B, Xie Y, Beidaghi M, et al. Two-dimensional, ordered, double transition metals carbides (MXenes). *ACS Nano*. 2015;9(10):9507-9516.

43. Yang J, Naguib M, Ghidiri M, et al. Two-dimensional Nb-based M4C3 solid solutions (MXenes). *J Am Ceram Soc*. 2015;99(2):660-666.

44. Yazdanparast S, Soltanmohammad S, Fash-White A, Tucker GJ, Brennecka GL. Synthesis and surface chemistry of 2D TiVC solid-solution MXenes. *ACS Appl Mater Interfaces*. 2020;12(17):20129-20137.

45. Tao Q, Dahlqvist M, Lu J, et al. Two-dimensional Mo1.33C1.33 MXene with divacancy ordering prepared from parent 3D laminate with in-plane chemical ordering. *Adv Funct Mater*. 2017;27(1):14949.

46. Dong Y, Shi H, Wu Z-S. Recent advances and promise of MXene-based nanostructures for high-performance metal ion batteries. *Adv Funct Mater*. 2020;30(47):2000706.

47. Aslam MK, Niu Y, Xu M. MXenes for non-lithium-ion (Na, K, Ca, Mg, and Al) Batteries and supercapacitors. *Adv Energy Mater*. 2020;11(2):2000681.
48. Aslam MK, Xu MW. A Mini-review: MXene composites for sodium/potassium-ion batteries. Nanoscale. 2020;12(30):15993-16007.

49. Lei Y-J, Yan Z-C, Lai W-H, et al. Tailoring MXene-based materials for sodium-ion storage: synthesis, mechanisms, and applications. Electrochem Energy Rev. 2020;3(4):766-792.

50. Zhang S, Han W-Q. Recent advances in MXenes and their composites in lithium/sodium batteries from the viewpoints of components and interlayer engineering. Phys Chem Chem Phys. 2020;22(29):16482-16526.

51. Zhao Q, Zhu Q, Liu Y, Xu B. Status and prospects of MXene-based lithium-sulfur batteries. Adv Funct Mater. 2021;31(21):2100457.

52. Zhang C, Cui L, Abdolhosseinzadeh S, Heier J. Two-dimensional MXenes for lithium-sulfur batteries. Infomat. 2020;2(4):613-638.

53. Zhu Q, Li J, Simon P, Xu B. Two-dimensional MXenes for electrochemical capacitor applications: progress and challenges. Energy Storage Mater. 2021;35:630-660.

54. Wang Y, Nian Y, Biswas AN, Li W, Han Y, Chen JG. Challenges and opportunities in utilizing MXenes of carbides and nitrides as electrocatalysts. Adv Energy Mater. 2020;11(3):2002967.

55. Naguib M, Kurtoglu M, Presser V, et al. Two-dimensional nanocrystals produced by exfoliation of Ti3AlC2. Adv Mater. 2011;23(37):4248-4253.

56. Alhabeb M, Maleks K, Anasori B, et al. Guidelines for synthesis and processing of two-dimensional titanium carbide (Ti1C7Tx MXene). Chem Mater. 2017;29(18):7633-7644.

57. Naguib M, Mashtilir O, Lukatskaya MR, et al. One-step synthesis of nanocrystalline transition metal oxides on thin sheets of disordered graphic carbon by oxidation of MXenes. Chem Commun. 2014;50(56):7420-7423.

58. Alhabeb M, Maleks K, Mathis TS, et al. Selective etching of silicon from Ti3SiC2 (MAX) to obtain 2D titanium carbide (MXene). Angew Chem Int Ed. 2018;57(19):5444-5448.

59. Ghidiu M, Lukatskaya MR, Zhao MQ, Gogotsi Y, Barsoum MW. Conductive two-dimensional titanium carbide ‘clay’ with high volumetric capacitance. Nature. 2014;516(7529):78-81.

60. Wu M, He M, Hu Q, et al. Ti1C7Tx MXene-based sensors with high selectivity for NH3 detection at room temperature. ACS Sens. 2019;4(10):2763-2770.

61. Liu F, Zhou A, Chen J, et al. Preparation of Ti1C2 and Ti1C3 MXenes by fluoride salts etching and methane adsorptive properties. Appl Surf Sci. 2017;416:781-789.

62. Liu DR, Wang LB, He Y, et al. Enhanced reversible capacity and cyclic performance of lithium-ion batteries using SnO2-interpenetrated MXene V2C architecture as anode materials. Energy Technol. 2020;9(2):2000753.

63. Wang X, Garnero C, Rochard G, et al. A new etching environment (FeF3/HCl) for the synthesis of two-dimensional titanium carbide MXenes: a route towards selective reactivity vs. water. J Mater Chem A. 2017;5(41):22012-22023.

64. Wu M, He Y, Wang L, Xia Q, Zhou A. Synthesis and electrochemical properties of V2C MXene by etching in opened/closed environments. J Adv Ceram. 2020;9(6):749-758.

65. Feng A, Yu Y, Jiang F, et al. Fabrication and thermal stability of NH4HF2-etched Ti3C2 MXene. Ceram Int. 2017;43(8):6322-6328.

66. Li T, Yao L, Liu Q, et al. Fluorine-free synthesis of high-purity Ti3C2Tx (T = OH−, O) via alkali treatment. Angew Chem Int Ed. 2018;57(21):6115-6119.

67. Luo J, Matios E, Wang H, Tao X, Li W. Interfacial structure design of MXene-based nanomaterials for electrochemical energy storage and conversion. Infomat. 2020;2(6):1057-1076.

68. Yu H, Wang Y, Jing Y, Ma J, Du C-F, Yan Q. Surface modified MXene-based nanocomposites for electrochemical energy conversion and storage. Small. 2019;15(25):1901503.

69. Xuan J, Wang Z, Chen Y, et al. Organic-base-driven intercalation and delamination for the production of functionalized titanate carbide nanosheets with superior photothermal therapeutic performance. Angew Chem Int Ed. 2016;55(47):14569-14574.
83. Sun Z, Yuan M, Lin L, et al. Selective lithiation–expansion–microexplosion synthesis of two-dimensional fluoride-free MXene. ACS Mater Lett. 2019;16(6):628-632.
84. Li Z, Ren Y, Mo L, et al. Impacts of oxygen vacancies on zinc ion intercalation in VOx. ACS Nano. 2020;14(5):5581-5589.
85. Fleischmann S, Mitchell JB, Wang R, et al. Pseudocapacitance: from fundamental understanding to high power energy storage materials. Chem Rev. 2020;120(14):6738-6782.
86. Wang C, Wei SQ, Chen S, Cao D, Song L. Delaminating vanadium carbides for zinc-on storage: hydrate precipitation and H2/Zn2+ co-action mechanism. Small Methods. 2019;3(12):1900495.
87. Li X, Li M, Yang Q, et al. In situ electrochemical synthesis of MXenes without acid/alkali usage in/for an aqueous zinc ion battery. Adv Energy Mater. 2020;10(36):2001791.
88. Li X, Ma X, Hou Y, et al. Intrinsic voltage plateau of a Nb2CTx MXene cathode in an aqueous electrolyte induced by high-voltage scanning. Joule. 2021;5(11):2993-3005.
89. Yu YX. Prediction of mobility, enhanced storage capacity, and volume change during sodiation on interlayer-expanded functionalized Ti3C2 MXene anode materials for sodium-ion batteries. J Phys Chem C. 2016;120(10):5288-5296.
90. Ling Z, Ren CE, Zhao MQ, et al. Flexible and conductive MXene films and nanocomposites with high capacitance. Proc Natl Acad Sci USA. 2014;111(47):16676-16681.
91. Luo J, Fang C, Jin C, et al. Tunable pseudocapacitance storage of MXene by cation pillaring for high performance sodium-ion capacitors. J Mater Chem A. 2018;6(17):7794-7806.
92. Luo J, Zhang W, Yuan H, et al. Pillared structure design of MXene with ultralarge interlayer spacing for high-performance lithium-ion capacitors. ACS Nano. 2017;11(3):2459-2469.
93. Wang C, Xie H, Chen S, et al. Atomic cobalt covalently engineered interlayers for superior lithium-ion storage. Adv Mater. 2018;30(32):1802525.
94. Zhang S, Ying H, Yuan B, Hu R, Han WQ. Partial atomic tin nanocomplex pillared few-layered Ti3C2T x MXenes for superior lithium-ion storage. Nano-Micro Lett. 2020;12(1):78.
95. Maughan PA, Tapia-Ruiz N, Bimbo N. In-situ pillared MXene as a viable zinc-ion hybrid capacitor. Electrochim Acta. 2020;341:136061.
96. Cheng W, Fu J, Hu H, Ho D. Interlayer structure engineering of MXene-based capacitor-type electrode for hybrid micro-supercapacitor toward battery-level energy density. Adv Sci. 2021;8(16):2100775.
97. Li X, Li M, Yang Q, et al. Vertically aligned Sn4+ preintercalated Ti3C2T x MXene sphere with enhanced Zn ion transportation and superior cycle lifespan. Adv Energy Mater. 2020;10(35):2001394.
98. Yang Q, Huang Z, Li X, et al. A wholly degradable, rechargeable Zn-Ti3C2T x MXene capacitor with superior anti-self-discharge function. ACS Nano. 2019;13(7):8275-8283.
99. Wang S, Wang Q, Zeng W, Wang M, Ruan L, Ma Y. A new free-standing aqueous zinc-ion capacitor based on MnO2-CNTs cathode and MXene anode. Nano-Micro Lett. 2019;11(1):70.
100. Shi J, Wang S, Wang Q, Chen X, Du X, Wang M, Zhao Y, Dong C, Ruan L, Zeng W. A new flexible zinc-ion capacitor based on 8-MnO2@Carbon cloth battery-type cathode and MXene@Cotton cloth capacitor-type anode. Journal of Power Sources. 2020;446:227345. http://doi.org/10.1016/j.jpowsour.2020.227345.
101. Li X, Ma Y, Yue Y, Li G, Zhang C, Cao M, Xiong Y, Zou J, Zhou Y, Gao Y. A flexible Zn-ion hybrid micro-supercapacitor based on MXene anode and V2O5 cathode with high capacitance. Chemical Engineering Journal. 2022;428:130965. http://doi.org/10.1016/j.cej.2021.130965.
102. Zhang N, Huang S, Yuan Z, Zhu J, Zhao Z, Niu Z. Direct self-assembly of MXene on Zn anodes for dendrite-free aqueous zinc-ion batteries. Angew Chem Int Ed. 2020;133(6):2897-2901.
103. Sun C, Wu C, Gu X, Wang C, Wang Q. Interface engineering via Ti3C2T x MXene electrolyte additive toward dendrite-free zinc deposition. Nano-Micro Letters. 2021;13(1):89.
104. Tian Y, An Y, Liu C, Xiong S, Feng J, Qian Y. Reversible zinc-based anodes enabled by zincophilic antimony engineered MXene for stable and dendrite-free aqueous zinc batteries. Energy Storage Mater. 2021;41:343-353.
105. Chen Z, Li X, Wang D, et al. Grafted MXene/polymer electrolyte for high performance solid zinc batteries with enhanced shelf life at low/high temperatures. Energy Environ Sci. 2021;14(6):3492-3501.
106. Liu Y, Jiang Y, Hu Z, et al. In-situ electrochemically activated surface vanadium valence in V2C MXene to achieve high capacity and superior rate performance for Zn-ion batteries. Adv Funct Mater. 2020;30(8):2008033.
107. Narayanasamy M, Kirubasankar B, Shi M, et al. Morphology restrained growth of V2O5 by the oxidation of V-MXenes as a fast diffusion controlled cathode material for aqueous zinc ion batteries. Chem Commun. 2020;56(47):6412-6415.
108. Tian Y, An Y, Wei H, et al. Micron-Sized nanoporous vanadium pentoxide arrays for high-performance gel zinc-ion batteries and potassium batteries. Chem Mater. 2020;32(9):4045-4064.
109. Li X, Li M, Yang Q, et al. Phase transition induced unusual electrochemical performance of V2CTx MXene for aqueous zinc hybrid-ion battery. ACS Nano. 2020;14(1):541-551.
110. Luo S, Xie L, Han F, et al. Nanoscale parallel circuitry based on interpenetrating conductive assembly for flexible and high-power zinc ion battery. Adv Funct Mater. 2019;29(28):1901336.
111. Zhu X, Cao Z, Wang W, et al. Superior-performance aqueous zinc-ion batteries based on the in situ growth of MnO2 nanosheets on V2CTx MXene. ACS Nano. 2021;15(2):2971-2983.
112. Shi M, Wang B, Chen C, Lang J, Yan C, Yan X. 3D high-density MXene@MnO2 microfilms for advanced aqueous zinc-ion batteries. J Mater Chem A. 2020;8(46):24635-24644.
113. An Y, Tian Y, Xiong S, Feng J, Qian Y. Scalable and controllable synthesis of interface-engineered nanoporous host for dendrite-free and high rate zinc metal batteries. ACS Nano. 2021;15(7):11828-11842.
114. Shi M, Wang B, Shen Y, et al. 3D assembly of MXene-stabilized spinel ZnMn2O4 for highly durable aqueous zinc-ion batteries. Chem Eng J. 2020;399:125627.
115. Liu C, Xu W, Mei C, Li M-C, Xu X, Wu Q. Highly stable H2V3O8/MXene cathode for Zn-ion batteries with superior rate performance and long lifespan. Chem Eng J. 2021;405:126737.
116. Xu G, Zhang Y, Gong Z, Lu T, Pan L. Three-dimensional hydrated vanadium pentoxide/MXene composite for high-rate zinc-ion batteries. J Colloid Interface Sci. 2021;593:417-423.
117. Zhang Y, Cao J, Li J, et al. Self-assembled cobalt-doped NiMn-layered double hydroxide (LDH)/V2CTx MXene hybrids for...
advanced aqueous electrochemical energy storage properties. *Chem Eng J*. 2022;430:132992.

118. Wang X, Wang Y, Jiang Y, et al. Tailoring ultrahigh energy density and stable dendrite-free flexible anode with Ti$_3$C$_2$T$_x$ MXene nanosheets and hydrated ammonium vanadate nanobelts for aqueous rocking-chair zinc ion batteries. *Adv Funct Mater*. 2021;31(35):2103210.

119. Zhao B, Wang S, Yu Q, et al. A flexible, heat-resistant and self-healable “rocking-chair” zinc ion microbattery based on MXene-TiS$_2$ (de)intercalation anode. *J Power Sources*. 2021;504:230076.

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