(REVIEW ARTICLE)

MXenes as promising active materials for divalent metal-ion batteries: A review of recent advances

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Abstract

MXenes are a new type of layered-dimensional (2D) materials consisting of transition metal carbides (nitrides and carbonitrides) that have received significant interest due to their intriguing properties. Its superior conductivity, large specific area, tunable chemistry, and layered structure have made it suitable for energy storage ever since its discovery. MXenes have shown great potential, especially in battery applications, including lithium-ion batteries, sodium-ion batteries, Li–S batteries, and zinc-ion batteries serving as excellent rate-performing electrode materials, good electron conductive substrates for active material, components for performance-enhancing composites and current collectors. Perhaps, the most important role MXene plays in electrochemical cells is serving as an active material for charge storage host. This review article discusses recent progress in the synthesis, characterization, and use of MXene as active materials in divalent ion battery applications with the aim of enhancing electrochemical performance. This review will also discuss the several charge storage mechanisms and performance enhancement of pure MXene or MXene-based composites in these battery systems. Lastly, the challenges and future prospects are summarized, offering an outlook on potential opportunities ahead for tailoring MXene as better active materials through tailoring microstructure.

Keywords: Mxene; Battery; Lithium; Magnesium; Zinc; Electrode; Energy

1. Introduction

The shift from fossil fuels like oil and gas to renewable energy marks a crucial energy revolution aimed at addressing global warming and transitioning to a sustainable, clean energy supply.[1-4] The development and utilization of renewable energy sources, such as solar, wind, tidal, hydro, and geothermal power, have become increasingly important in reducing greenhouse gas emissions and mitigating climate change. However, the intermittent nature of these energy sources poses challenges in meeting the stability and reliability requirements of the power grid. To overcome this, energy storage devices have become essential technologies for storing and redistributing electricity generated from renewable sources, ensuring a more stable and reliable energy supply. In particular, electrochemical energy storage solutions have emerged as the mainstream choice for these applications due to their high energy density, long service life, environmental benefits, and absence of memory effect. The lithium-ion battery is widely accepted type but due to dwindling raw material, cost and safety concerns, alternative metal ions have been considered including magnesium, zinc, calcium, and aluminum due to their abundance in nature. However, the development of multivalent ion batteries, such as Mg^{2+}, Zn^{2+}, Ca^{2+}, and Al^{2+}, is significantly hindered by several challenges, including structural deterioration and capacity decay, poor electrode compatibility with non-aqueous organic-based electrolytes, low electrochemical reversibility, and particularly slow ion diffusion kinetics.[5, 6] The slow ion diffusion kinetics is due to the large radius of the hydrate multivalent ion in suitable solvent.[7] Because of this, single valent metal ions like potassium (K^+) and sodium (Na^+) that possess lower desolvation energy and can form smaller solvation ions are more preferred in

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combination with their abundance in the earth's crust. Sodium and potassium are the 6th and 7th most abundant element in the earth's crust with sodium and potassium both consisting of greater than 2.0% of the top component of the lithosphere providing the advantage of low cost. [8, 9] However, batteries made from storage of these ions are still plagued in real life applications by large volume expansion of active materials during charging and discharging, largely reducing the cycle stability and energy density. These challenges produces the need to develop and design better active material for battery anode and cathodes to maximize the device performance of metal ion batteries. The ongoing expansion of different electrode materials, which are critical to battery performance, has been a major research focus in recent years. The aim is to identify and implement cost-effective alternative materials that can provide highly reversible ion storage capacity, high power and energy density and extended cycle life.[10]

Several materials have been developed for battery systems to combact issues related to electrochemical cells including thermal runaway, dendrite formation, unstable formation of solid and electrolyte interface.[11] For example, lithium titanium oxide also known as LTO have been employed in lithium-ion batteries to mitigate the formation of dendrites but possesses extremely low conductivity and poor lithium ion diffusivity. Alloying metals like silicon have also been explored as improved anode materials due to low discharge voltage and higher theoretical capacity but these also suffer from volume change during cycling. To mitigate the volume change, nanostructures of these materials have been developed for example the yolk shell structure consisting of Si and graphene.[12] Although the yolk shell structure improved capability and cycle stability, it demonstrated poor coulombic efficiency. Nanocomposites have also been introduced to improve cathode performance. $Fe/LiF/Li_2O$ nanocomposite have been used to mitigate metal ion loss and enhance power density in lithium ion batteries serving as a cathode prelithiation material.[13] Polyanionic compounds have also been introduced as electrode materials due to their structural diversity and stability especially for sodium-ion batteries. Olivine Sodium iron phosphate ($NaFePO_4$) have been used in fabrication of cathode materials due to their high theoretical capacity (154 mA h g^{-1}).[14] This structural analog to $LiFePO_4$ is obtained it's delithiation and subsequent sodiation. Although olivine $NaFePO_4$ offers enhanced performance for NiB due to its higher theoretical capacity among polyanionic phosphates, its lack of thermodynamic stability and the need for complex ion exchange processes to derive it from olivine $LiFePO_4$ hinder its practical application.[15] Even more disappointingly, it's thermodynamic state, maricite $NaFePO_4$ is considered electrochemically inactive due to insufficient diffusion channels for metal ions.

In the last two decades, there has been a notable surge in interest surrounding the development of alternative electrode materials using organic small molecules and polymers. These materials are highly regarded for their tunable properties, cost-effectiveness, abundance of raw materials, potential for recyclability, and comparatively low toxicity. For example, microporous organic polymers (MOPs) have been introduced into battery systems due to their extremely high surface areas, ranging from approximately 50 to 4000 m^2/g, which provide a large contact area with the electrolyte solution.[16] Organic radical batteries (ORBs) have also been developed and are renowned for their exceptional cycling stability at extremely high rates. Wang et al. introduced a post-synthetic method to crosslink thick PTMA cathodes (15–25 mm) with high capacity and cycling stability, retaining 77% of their capacity at a 10 C rate. Although possessing fast kinetics, ORBs suffer from poor electrical conductivity due to localized electron density on the nitroxide radical. 2D nanomaterials have also been explored for improving the performance of battery systems due to their large active surfaces and open ion diffusion channels, which enable fast transport and easy storage of metal ions. There are three different types of insertion materials for metal ions in battery applications: one-dimension (e.g Olivine based structures), two-dimensional materials (e.g Graphene based structures, and three-dimensional (e.g Silicon based structures). Amongst these, 2D materials are more promising due to their open ion transport channels, reducing ion diffusion distances and faster ion transport. The interlayer spacing of 2D nanomaterials can be easily controlled post-sythensis or pre-synthesis through deliberate intercalation of ions and molecules, widening the gap of the weakly bonded layers, increasing the electrode's tolerance to volume changes during cycling. 2D materials can also serve as functional components of electrode composite materials. For example, Cui et al, ultilized heat treatment processing to prepare a three-dimensional conductive network of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) rods wrapped in reduced graphene oxide (rGO) sheets at a ∼ 9% of rGO by weight. The composite retained 64% of its capacity at 1.0 A g^{-1} (relative to 172 mA h g^{-1} at 0.1 A g^{-1} obtaining a 63% improvement in capacity and a 28% improvement in capacity retention than batteries made from pure PTCDA.[17] Pristine 2D materials themselves can also serve as electrode materials due to their high electronic conductivity. Fang et al. developed a solution deposition method to synthesise 2D mesoporous graphene nanosheets, providing a high surface area for lithium ion adsorption and intercalation.[18] Apart from service as pure or hybrid electrode materials , 2D materials can also serveas functional substrates for incorporating various active materials improving enhancing the overall performance of the electrochemical cell. The list of common 2D materials that have been explored for rechargeable batteries include not limited to transition metal dichalcogenides (TMDs), Phosphorene, hexagonal boron nitride, MXenes and graphene and its derivatives. MXene is one of the 2D materials explored for various types of electrochemical energy storage systems include electrochemical capacitors (ECSs) and rechargeable battery (RBs). Mxenes are a new family of 2D transition

metal carbides/nitrides discovered in 2011 by Gogotsi et al by accidentally etching Al layer from three-dimensional Titanium aluminum carbide (Ti_3AlC_2) MAX phase with hydrofluoric acid (HF) forming a hexagonal structure of Ti_3C_2.[19] Since its discovery, MXene have received significant amount of attention in the material science field mostly due to atomic level thickness, excellent electronic conductivity, extremely large surface area and, dispersibility in a wide range of solvents and ease of surface chemistry tunability. These unique properties have made MXenes attractive in catalysis, photonics, energy storage, electromagnetic interference (EMI) shielding, membranes and water treatment. In terms of energy storage, MXene have shown great promise in ECs and RBs. Due to it's open channel structure unlike it's precursor material, MXene have been used as an excellent electroactive material for supercapacitors. In addition, to these unique properties in-situ studies have shown that the electrochemical cycling leads to only minor changes in the interlayer spacing making it an ideal electrode material for SC application that requires little or no phase change. MXene has also shown potential in battery applications due to its unique chemistry layered structure and high electronic conductivity. Density functional theory (DFT) first predicted this potential, demonstrating how Li+ can be stored by $Ti_3C_2T_x$, leading to the formation of $Ti_3C_2Li_2$.[19] Beyond Li-ion batteries, MXenes have been utilized in Na-, K-, Mg-, and Al-ion batteries, which are increasingly gaining recognition as emerging low-cost technologies for renewable energy storage. This review explores the application of MXene materials in various battery technologies. It provides a brief overview of the synthesis strategies and properties of $Ti_3C_2T_x$, followed by an in-depth examination of $Ti_3C_2T_x$-based materials in electrochemical cells, including but not limited to Li-ion, Na-ion, K-ion, Mg-ion, and Al-ion batteries.
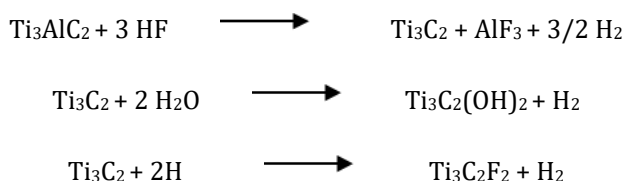
2. MXene structure and synthesis

MXenes are a new class of two-dimensional (2D) nanomaterials that consists of early transition carbides, nitrides or carbonitrides. The general formula for MXene is given as $M_{n+1}X_nT_x$, where M represents an early transition metal, X represents carbon or nitrogen, n is between 1 and 3, and Tx represents a surface terminal group. Functional groups that can incorporated on the surface of MXene sheets include fluorine hydroxyl group and oxygen. Since the introduction of graphene and its remarkable properties, exploring two-dimensional (2D) materials has become a significant focus in materials science and MXene, in particular, has rapidly gained increased attention within a relatively short 12-year period since its introduction.[20] MXenes are synthesized by selectively etching their respective multilayer MAX phases, which are 3D dimensional in structure, often utilising etchants such as HF and other fluorine-based solid acids. MAX phases are hexagonal compounds that comprise metal carbides, nitrides or carbonitrides, with a general formula of $M_{n+1}AX_n$ where n is between 1 and 4. In this formula, M and X represent the exact definition as in MXene, and A represents elements from groups 13 and 14 of the periodic table.[20, 21] Some structural features, including the hexagonal structure of the precursor, are transferred to the corresponding MXenes, which consist of an HCP (hexagonal closed-packed) crystal structure, and space group $P6_3/mmc$ space group where the X atoms occupy the octahedral sites. The atomically thin single flakes of MXene display a hexagonal lattice, with sixfold symmetry and a rhombus unit cell in the top view, resembling that of graphene and derivatives but terminated by functional groups referred to as T_x.[22] In the interest of simplicity, Tx represents mixed surface terminations. This is because, in most synthesis protocols conducted in a fluoride-based solution, the transition metal surfaces of MXene are terminated by -O, -OH, and also -F which is donated from the acid.[23] Unlike other two-dimensional materials, the functional termination groups in MXene do not rely on controlled reactions; instead, they arise from the exfoliation process itself. The selection of precursor MAX Phase, etching conditions, etchant, intercalants, and subsequent surface termination collectively influence a MXene's composition and, thereby, its properties. The family of MAX phases is extensive and continually expanding, with over 70 confirmed compositions to date. Notable examples include Ti_2AlC and Ti_3AlC_2. These materials have garnered significant attention in the scientific community due to their unique hybrid nature, which combines characteristics typically associated with both ceramics and metals.

In addition to random solid solutions on the M site, recent years have seen a growing focus on MAX structures with ordered alloying of M elements, leading to the discovery of the first ordered MAX phase alloy, $(Cr_{2/3}Ti_{1/3})_3AlC_2$, about 10 years ago.[24] This compound is easily reduced to a phase that possess out of plane order, M_3AX_2 e.g Ti_3AlC_2 and Ti_3SiC_2 where of single M are interleaved with layers of A and X. This led to the development of M_4AX_3 with a similar out of plane structure for example, $Mo_2Ti_2AlC_3$ where leading to the introduction of out of plane MXenes where ordering is achieved by introducing a second transition metal element, which disrupts the stacking of the first metal element, leading to a more energetically favorable structure.[25] The chemical composition and ordering in MAX phases and their derived MXenes significantly influence material properties. For instance, while Ti_3AlC_2 exhibits metallic conductivity, replacing the outer Ti layers to form the structurally similar Mo_2TiC_2Tx results in a material with semiconductor-like characteristics.

3. MXene synthesis and structure

Single-layer MXene flakes are synthesized through a selective etching process, that involves three key steps.: precursor synthesis, etching, and delamination. This top-down approach has been in use since the discovery of Mxenes in 2011. The entire process begins with the synthesis of layered 3D MXene precursors. These precursors, often composed of MAX or sometimes non-MAX phase materials, have interesting crystal structures and are mainly composed of multiple layers of "A" atoms or carbide strata composed of A-elements (like $M_nA_3X_{n+2}$), as mentioned earlier. The resulting 2D materials are formed through a structure where n+1 layers of "M" alternate with n layers of "X," providing a favorable avenue for a wealth of surface terminations. [26]. In the second step, the A atom layers are selectively etched out because of the stronger M-X bonds and relatively reactive A layers, which are also weakly bonded.[27, 28] This etching reduces the precursor's composition, forming MXene multilayers that are loosely bonded together by weak van der Waal forces.[26, 29] In the first report of this process, the authors successfully etched Ti_3AlC_2 and suggested the following mechanism representing the removal of the Al layer.[19]

$$Ti_3AlC_2 + 3\ HF \longrightarrow Ti_3C_2 + AlF_3 + 3/2\ H_2$$

$$Ti_3C_2 + 2\ H_2O \longrightarrow Ti_3C_2(OH)_2 + H_2$$

$$Ti_3C_2 + 2H \longrightarrow Ti_3C_2F_2 + H_2$$

In the MAX phase, the M-X bonds are mainly covalent and strong ion bonds involving the complete transfer of electrons, which is attributed to great binding strength. This is in contrast with the bonds between M and A, which are mainly metallic and have much weaker binding strength. [26] When etching the A atomic layer, the comparatively weaker M-A bonds are broken. This leads to undercoordinated M surfaces, which are rapidly saturated by the Tx species from the etchant. [29, 30] In the last step, the multi-layered MXene sheets are delaminated through a chemical process or mechanical agitation, resulting in single-to-few layered MXene sheets. [26, 31, 32] Immediately after the etching process, washing the material to eliminate any leftover acid and possible byproducts is necessary to reach a safe pH level of around 5-6 [33]. This is important because, depending on the synthesis protocol, not all of the MAX phase will be reacted, leaving the process yield significantly less than 100%.

In the initial years following the discovery of MXene in 2011, only the synthesis of multilayer MXene was achievable through wet-chemical etching using HF. Various types of MXene were first synthesised in this 3D layered form. [27, 28, 33, 34] It was not until 2013 that single-layer MXene flakes were successfully isolated for the first time by intercalating large organic molecules, which helped break the weak van der Waals forces between the multilayer sheets, leading to their delamination into atomically thin monolayer flakes. This led to the introduction of the first group of intercalants and delamination agents for MXene, an ever-increasing group of compounds, and paved the way for numerous methods to synthesize single or few-layer flakes, enabling researchers to exploit the potential and inherent properties of MXene to the fullest potential. [31, 33] It is crucial to highlight that in addition to nanosheets, other structures, such as scrolls and MXene nanotubes, have been observed through electron microscopy after sonication. [27] For titanium and vanadium-based MXene, experiments have demonstrated that the functional groups are randomly distributed, agreeing with the predictions of computational quantum mechanics. [35] However, there is a limited understanding of the surface termination mechanism, and to fully substantiate these simulation forecasts, more experimental research centered on functional group chemistry and control is important. [36]

As MXene research progressed, several modifications were proposed in the acid etching process used for MXene production to resolve several issues faced during the synthesis process. Atomic scale inhomogeneities, including internal and external defects have been indetified in MXene after acid etching. These defects can be inherited from the precursor bulk MAX phases, which were less common, or introduced during the etching and delamination processes, which were much more frequent. [37, 38] These defects, typically revealed through scanning tunneling microscopy (STEM), can be vacancies and adatoms and are commonly formed through ultrasonication or etching with high amounts of acids. This led to the introduction of the minimally intensive layer delamination method (MILD) that uses a lithium-based salt to synthesize the required HF acid in situ, so sonication is no longer required for delamination. The introduction of this method was revolutionary for MXene synthesis because it expanded the scope of research into Ti3C2Tx MXene. This technique not only facilitates investigations into the material's electronic, optical, and size-dependent properties but also enhances its scalability and production efficiency by enabling easier access to high-quality and defect-free samples. Apart from LiF, other flouride salt have been used including NH_4HF_2, $NaBF_4$ and NH_4F, to produce in situ HF.[39] However, defects are not the only challenge in MXene synthesis. For instance, the harmful effects of fluorine terminations on various applications have driven research toward developing fluorine-reduced and

fluorine-free synthesis protocols.[40] Fluoride-based synthesis of MXene are environmentally unfriendly and also the presence of inert fluorine in the surface termination of MXene limit electrochemical performance. Yang et al. demonstrated an efficient and high yield fluoride-free etching method based on the anodic corrosion of Ti_3AlC_2 in a binary aqueous electrolyte.[41]

4. Properties of MXene

MXene are known for the unique and excellent mechanical, electrical, optical and thermal properties. The mechanical properties of MXenes largely depends on the it's acquired fucntional groups during synthesis as predicted by density function theory where O terminated MXenes have very high stiffness, but MXenes terminated by other groups F and OH show lower elastic stiffness and the non-terminated MXene being less flexible.[42] Guo and colleagues experimentally found that functionalization reduces the Young's modulus of Ti_2C. However, the functionalized Ti_2C can endure a greater strain compared to its non-functionalized counterpart and even graphene.[43] The chemical composition also largely affects the mechanical properties of delaminated MXene. Using first principle calculation Yorulmaz et al, systematically investigated the dynamical and mechanical stability of several MXenes. The authors found that among all $Ti_{n+1}C_n$ compounds, Ti_2C has the highest Young's modulus and an elastic constant nearly twice that of molybdenum disulfide (MoS_2).[44] Recent findings by Naguib et al. revealed that $Ti_3C_2T_x$ undergoes oxidation when exposed to air, CO_2, or pressurized water. This oxidation process results in the formation of anatase TiO_2 nanocrystals embedded within amorphous carbon sheets, creating a TiO_2-C hybrid structure.[45] Likewise, Li et al. discovered that $Ti_3C_2T_x$ can react with O_2 to produce TiO_2 in either rutile or anatase phases. Unlike the TiO_2-C hybrid structure, the resulting anatase nanocrystals were uniformly distributed across the 2D Ti_3C_2 layers.[46]

Thus far, theoretical computations have reported the electronic, dielectric, magnetic, elastic, thermoelectric, and optical properties of MXene. However, only a limited number of experiments have provided strong validation for these predictions. MXene species, such as $Ti_{n+1}X_n$, exhibit metallic behavior. However, their metallic properties tend to diminish with increasing n values, attributed to the formation of additional Ti-X bonds. When considering X atoms, titanium nitrides display greater metallic properties compared to titanium carbides, primarily because nitrogen atoms have one more electron than carbon atoms. In contrast, terminated MXene sheets can exhibit characteristics ranging from narrow-band-gap semiconductors to metallic behavior, depending on the type and orientation of their surface groups. Lee et al. investigated the effects of applied strain on the band gap of Sc_2CO_2, as strain can change interatomic distances and the relative positions of atoms within a material. As the tensile strain increases, the band gap gradually decreases.[47] MXenes have excellent conductivity, with a metallic conductivity of up to $\sim$24,000 S cm^{-1}. The structure of MXene contains many transition metal elements, for example, titanium and molybdenum, which usually have high conductivity, forming conductive channels in the MXene structure and promoting electron transmission, thereby improving the overall conductivity of MXene.[48]

5. Electrochemical Properties of MXene

MXene materials are distinguished by their unique layered architecture, which makes them highly attractive in advanced materials research. This structure is composed of alternating layers of transition metal carbides or nitrides, interspersed with intercalated species. The interlayer spacing is a critical factor, as it facilitates the insertion and extraction of ions—an essential mechanism for energy storage applications. For high-quality MXenes, the intercalation process is often an essential step that greatly influences their properties, and it has been demonstrated that using tetrabutylammonium hydroxide (TBAOH) resulted in MXenes with the largest interlayer spacing, measuring 16.58 Å, which resulted in greater volumetric and gravimetric capacitance. MXenes offer adjustable interlayer spacing, which can be optimized to enhance the diffusion of specific ions, such as Li^+ or Na^+, in battery applications. Additionally, their versatile surface terminations enable tailored electrochemical properties, allowing precise control over capacitance and potential windows. Gaining insights into the relationship between ion size, surface chemistry, and interlayer spacing is crucial for advancing MXene-based energy storage systems. In practical applications, the interaction between MXenes and electrolytes plays a vital role, as redox processes on MXene surfaces can influence electrolyte stability and capacity. Exploring MXene-electrolyte interactions and optimizing electrolyte compositions are essential steps toward developing reliable and high-performance devices. Strategies such as functionalization, hybridization, and composite formation have been employed to enhance electrochemical performance. Surface functionalization, in particular, alters the electrical properties and wettability of MXenes, thereby affecting their charge storage behavior.

6. MXene Zinc-ion Batteries

Since zinc anodes were first introduced in 1799, zinc-ion batteries (ZIBs) have emerged as promising energy storage devices due to their safety, affordability, abundance, and high performance. This is attributed to the biocompatibility of zinc, its high theoretical capacity (819 mAh g^{-1} and 5,851 Ah L^{-1}), and the low redox potential of the Zn^{2+}/Zn couple (−0.76 V vs. SHE).[49] Significant progress has been made in the application of MXene materials for zinc-ion storage devices over the past two years. Advances in understanding the zinc-ion storage mechanisms of MXenes have led to notable improvements, enabling more diverse applications. These developments highlight the immense potential of MXenes for delivering high-performance zinc-ion storage systems. For several years, MXene has been regarded as relying on an adsorption-desorption mechanism on its surface for zinc-ion storage. However, pure MXene synthesized through the conventional HF etching method has shown low reversible capacity in zinc-ion batteries (ZIBs), as evidenced by cyclic voltammogram (CV) curves. In aqueous electrolytes, the cyclic voltammogram (CV) of MXene typically displays a rectangular shape without distinct redox peaks. This behavior contrasts with its performance in organic electrolytes, suggesting that pure MXene stores zinc ions primarily through a double-layer capacitor mechanism, potentially supplemented by a surface pseudocapacitive reaction.[50] Additionally, Song and colleagues developed a carbon nanotube (CNT)-delaminated V$_2$C MXene (DV$_2$C@CNT) and utilized it in a zinc-ion capacitor (ZIC). Their study revealed the co-intercalation behavior of zinc ions and hydrogen ions during the cycling process.[51]

In contrast to rechargeable alkaline Zn–MnO$_2$ batteries, zinc-ion batteries (ZIBs) face challenges such as the formation of irreversible zinc compounds, including Zn(OH)$_2$ and ZnO, along with dendrite growth. These issues significantly shorten the cycle life of ZIBs. In 1986, Yamamoto et al. developed rechargeable aqueous zinc-ion batteries (ZIBs) utilizing neutral or mildly acidic electrolytes, such as ZnSO$_4$, which effectively mitigate dendritic zinc deposition.[52] One of the primary challenges for aqueous ZIB cathodes is the electrostatic interaction between host materials and Zn^{2+} ions. To address this, various carbon-based materials have been employed as conductive components in combination with MnO$_2$ for aqueous ZIBs.[53] Compared to the previously studied carbon nanomaterials for ZIBs, 2D MXenes offer richer surface functionality, exceptional metallic conductivity, remarkable hydrophilicity, and a higher density of 4 g cm^{-3}. Recently, Minjie Shi et al. proposed that a 3D micro-flower-like structure not only delivers outstanding structural stability but also improves electrical conductivity when paired with highly electroactive MnO$_2$ during cycling. [54]

Manganese-based, vanadium-based, Prussian blue, and conductive organic materials are among the most studied cathode materials for ZIBs. Of these, manganese- and vanadium-based oxides are particularly prominent due to their high working voltage and excellent theoretical capacity for zinc storage. However, manganese-based oxides often face challenges such as low conductivity and irreversible manganese dissolution, resulting in poor rate performance and limited cycle stability. MXenes, a novel class of two-dimensional layered materials, offer unique advantages as cathode materials for ZIBs. They feature diverse structures, exceptional conductivity, abundant surface functional groups, fast ion diffusion kinetics, and robust mechanical properties. Their hydrophilic surface groups enhance electrolyte wettability, facilitating efficient electrochemical reactions. The 2D layered structure and high conductivity provide a stable and conductive platform for manganese- and vanadium-based composites, improving both cycle stability and rate performance. Furthermore, 3D MXene architectures accelerate zinc-ion transport, while their rich surface terminations deliver high activity and a wide voltage window, making them highly promising for ZIB applications.[55]

Ti$_3$C$_2$T$_x$ MXenes functionalized with Br, I, and combinations of halogens have been utilized as cathodes for aqueous ZIBs. Hybridization near the surface of halogenated MXenes enhances their surface chemistry, while polar bonds near the surface generate van der Waals forces between MXene layers, resulting in an accordion-like structure. Notably, Ti$_3$C$_2$Br$_2$ and Ti$_3$C$_2$I$_2$ exhibit higher specific capacities of 97.6 mAh g^{-1} and 135 mAh g^{-1} at 0.5 Ag^{-1}, respectively, compared to Ti$_3$C$_2$(OF), which delivers 51.7 mAh g^{-1} at the same rate.[56] Ti$_3$C$_2$Br$_2$ and Ti$_3$C$_2$I$_2$ also demonstrate exceptional rate capability and cycling stability, delivering impressive discharge capacities of 120 mAh g^{-1} and 181 mAh g^{-1} at a current density of 0.25 A g^{-1}, respectively. Even at a high current density of 15 A g^{-1}, they retain 45% and 56% of their capacities, highlighting their robust performance.[56] The electrochemical activity of –Br and –I functional groups enables reversible redox reactions that are not typically observed in MXenes with conventional –O and –F terminations. Compared to –F- and –Cl-terminated MXenes, halogen-sealed MXenes (excluding –Cl) exhibit partial pseudocapacitance, as evidenced by distinct redox behavior. Recent findings indicate that applying a higher scanning voltage in Nb$_2$CT$_x$/Zn batteries enhances the activation of various zinc-ion storage sites.This process improves the storage capabilities of pure MXene batteries and facilitates the Zn^{2+} intercalation and deintercalation mechanism. [57]

Currently, zinc metal serves as the primary anode material for ZIBs. With a reduction potential of -0.76 V (vs. SHE), zinc undergoes a dissolution and deposition process of Zn^{2+} on its surface when electrochemically charged or discharged in neutral or mildly acidic aqueous solutions.[58] Despite its advantages, zinc metal faces several challenges in practical applications: (1) water-based electrolytes can corrode zinc metal during cycling; (2) zinc is susceptible to forming

uneven dendrites during deposition and stripping, potentially causing failure; and (3) hydrogen evolution during deposition/stripping, along with local pH fluctuations, can lead to the formation of insulating zinc hydroxide or zincate, which passivates the fresh zinc surface. To address these issues, current research focuses on zinc anode protection, electrolyte optimization, and separator design.[55] MXenes offer several advantages as substrates for zinc anodes. Their excellent electron conductivity and ion diffusivity support rapid electrochemical kinetics during zinc plating and stripping. Additionally, the lattice compatibility between MXenes and zinc metal promotes uniform nucleation and deposition. The rich surface terminal groups on MXenes serve as zincophilic sites, further facilitating even nucleation and deposition of zinc. With versatile surface chemistry and good dispersion in solutions, MXenes can also be processed into various porous structures. Based on these advantages, recent research on MXenes for zinc anodes has focused on intercalation, surface terminal modifications, and morphology design.

7. MXene in Magnesium-ion Batteries

Magnesium is abundantly available worldwide, and its cost is approximately 1/24th that of lithium, providing a solid foundation for the advancement of magnesium-ion batteries (MIBs). Unlike lithium-ion batteries (LIBs), MIBs are not prone to dendrite growth, which enhances their safety by reducing the risk of short circuits caused by dendrite formation. From an energy perspective, the divalent nature of Mg^{2+} allows it to transfer two electrons simultaneously, effectively doubling the theoretical capacity of MIBs compared to LIBs under similar conditions.Furthermore, MIBs have the characteristics of high theoretical capacity (2205 mAh g−1), long service life, high energy storage capacity, and large volumetric energy density which are of great significance for the development of environmentally friendly energy storage system. [59] Given these advantages, MIBs have the potential to replace LIBs and hold promise for a bright future. However, MIB systems still face several challenges. One major issue is the strong electrostatic forces associated with divalent Mg^{2+} ions, which lead to strong interactions with the host material. This, in turn, results in sluggish diffusion kinetics and limited reversible capacity.

Current research on MXene's magnesium storage performance mainly focuses on Ti_3C_2. However, density functional theory (DFT) calculations suggest that N-based MXenes may be more promising candidates, offering higher theoretical capacities. For instance, single-layer V_2N and single-layer Ti_2N are predicted to achieve theoretical capacities of 1850 mAh/g and 1874 mAh/g, respectively.[60] The greater electronegativity difference between Mg and N may account for this behavior. Magnesium storage efficiency in MXenes is heavily influenced by adsorption energy, where effective adsorption requires a negative adsorption energy. A higher absolute value indicates a stronger interaction. Unlike Li and Na, Mg is capable of multilayer adsorption on MXene surfaces, providing notable theoretical advantages. The magnesium storage capacities in bare Ti_2C, V_2C, Ti_3C_2, and Nb_2C are 1050, 1000, 812, and 729 mAh/g, respectively, which contrasts sharply with the capacities observed for Li and Na.[61] Xie et al. investigated the reaction mechanism of Mg^{2+} in MXene materials. When MXene is utilized as a cathode material for MIBs, Mg^{2+} is initially adsorbed onto negatively charged O-MXene through electrostatic interactions, driven by its negative surface adsorption energy. In contrast, OH-MXene, which exhibits positive adsorption energy, and F-MXene, which lacks stability, are excluded from consideration.[62] Due to the minimal repulsion between Mg^{2+} ions and transition metal atoms in MXene, along with the strong shielding effect of negative electron clouds, Mg^{2+} is the only polyvalent metal ion capable of forming two complete adsorption layers. During the reaction process, the lower adsorbed Mg^{2+} ions undergo intercalation and deintercalation between MXene layers, while the upper adsorbed Mg^{2+} ions participate in deposition and dissolution mechanisms. This dual-layer adsorption significantly enhances the magnesium storage capacity of MXene. A notable advantage is that Mg^{2+} ions in the adsorption layer do not form a passivation layer, unlike magnesium metal during deposition, facilitating uninterrupted reactions. Additionally, in the presence of Mg, O-MXene undergoes a transformation reaction, decomposing into bare MXene and magnesium oxide. While bare MXene exhibits better ion diffusion properties compared to O-MXene, the lack of stable electrolytes has hindered experimental validation of this transformation reaction. Moreover, the occurrence of the dissolution and deposition reactions in the second adsorption layer remains uncertain. It is important to recognize that synthesized MXene materials inherently possess terminal groups, which result in polyvalent metal-ion diffusion performance that is inferior to that of alkali metal ions. This limitation slightly reduces their rate performance. Therefore, enhancing magnesium intercalation and deintercalation by optimizing adsorption and diffusion processes is critical for improving the overall utilization and performance of MXene materials.

MXene has been extensively investigated for applications in lithium-ion batteries (LIBs), lithium-sulfur batteries, supercapacitors, and other energy storage systems. However, its potential as a cathode material for magnesium-ion batteries (MIBs) remains in the early stages of exploration. Current strategies to enhance the performance of MXene in MIBs focus on optimizing material composition, improving structural design, and expanding the range of MXene derivatives. In addition to optimizing layer spacing, constructing three-dimensional (3D) structures to provide abundant active sites has emerged as an effective morphological optimization approach. For instance, Zhao et al.

developed a 3D macroporous $Ti_3C_2T_x$ film with high porosity (90%), large specific surface area, and excellent conductivity using a template sacrifice method. Premagnesium ($Mg_{0.21}Ti_3C_2T_x$) was successfully achieved by immersing the 3D macroporous $Ti_3C_2T_x$ film in an all-phenyl complex (APC) electrolyte. This 3D macroporous $Ti_3C_2T_x$ structure demonstrated stable performance, retaining a capacity of 50 mAh/g after 60 cycles at 1 A/g.[63] Material compositing is another widely used strategy for improving electrode performance. It leverages the synergistic effects between different materials to significantly enhance overall properties. Such composites often exhibit superior electrochemical performance, including higher rate capabilities and improved cycling stability. MXene-based materials utilized as cathodes for MIBs can generally be divided into two main categories: carbon-based composites and composites based on transition-metal oxides and chalcogenides (TMOCs).[64]

Although MIBs offer notable advantages over LIBs in terms of theoretical capacity and the abundance of magnesium on Earth, recent studies have primarily utilized bulk magnesium as the anode material. However, the use of excessive magnesium results in a significantly lower energy density for MIBs compared to conventional LIBs (approximately 700 Wh/L). This design approach not only helps to substantially reduce manufacturing costs but also optimizes energy density.Li et al. demonstrated through theoretical calculations and experimental testing that $Ti_3C_2T_x$ MXene is a promising candidate as a current collector for anode-free magnesium batteries. The flexible $Ti_3C_2T_x$ MXene film effectively accommodates volume changes during cycling, while its rough surface facilitates strong adhesion between Mg deposition and the collector. Theoretical studies further indicated that the surface -O terminal groups on $Ti_3C_2T_x$ MXene exhibit a high affinity for magnesium atoms, promoting efficient magnesium deposition. Additionally, the low lattice mismatch between $Ti_3C_2T_x$ MXene and metallic Mg plays a crucial role in enabling uniform nucleation and horizontal growth of magnesium.[65] Li et al. also explored the use of $Mo_2Ti_3C_2$ MXene as a current collector for anode-free magnesium batteries. $Mo_2Ti_3C_2$ MXene offers several advantages, including a larger interlayer spacing, higher content of -O terminal groups, greater Young's modulus, reduced film thickness, and superior electrical conductivity. Notably, $Mo_2Ti_3C_2$ MXene exhibited a compact structure instead of a porous one, which sets it apart from other MXene materials.[66]

In addition to serving as an active electrode material, MXene is highly effective as a substrate material due to its layered structure and excellent electrical conductivity. When combined with magnesium cathode active materials, it enhances the performance of both components. MoS_2, a typical magnesium storage cathode material, often suffers from low capacity and poor cycling stability. To address these issues, Xu et al. incorporated $Ti_3C_2T_x$ as an "enhancer" into MoS_2 through an in situ hydrothermal method, forming a $MoS_2/Ti_3C_2T_x$ composite structure. In this process, MXene adsorbed Mo^{4+} ions as nucleation sites, allowing the gradual growth of thin, petal-like MoS_2 layers on the $Ti_3C_2T_x$ substrate. This unique morphology provides abundant exposed active sites for Mg^{2+} storage while also creating additional channels to enhance Mg^{2+} diffusion kinetics.[67] Li et al. synthesized TiS_2/Ti_3C_2 composites through hydrothermal assembly, utilizing Ti_3C_2 MXene as an ideal substrate. Compared to pure TiS_2 cathode material, the TiS_2/Ti_3C_2 composite exhibited a cumulative capacity of 97 mAh g^{-1} for MIBs at a current density of 50 mA g^{-1}. Similarly, Liu et al. developed $Ti_3C_2/CoSe_2$ heterojunctions by first growing a MOF (ZIF-67) structure in situ on Ti_3C_2, followed by selenization. Following a mechanism similar to that proposed by Xu et al. [89], the $Ti_3C_2/CoSe_2$ composite, used as a cathode material for MIBs, demonstrated outstanding cycling stability (over 500 cycles) and excellent rate performance, delivering 75.7 mAh g^{-1} at 1000 mA g^{-1}.

8. Other applications of MXene in Divalent or Multivalent ion Batteries

Multivalent ions, such as divalent Ca^{2+}, Mg^{2+}, and Zn^{2+}, as well as trivalent Al^{3+}, have been proposed as promising alternatives to monovalent Li^+ for next-generation energy storage systems. Unlike lithium, early studies suggest that multivalent metals, including magnesium and calcium, can be deposited uniformly from suitable electrolyte solutions with minimal dendritic growth. This characteristic makes multivalent metallic anodes a viable replacement for graphite anodes commonly used in lithium-ion batteries, offering significantly higher gravimetric and volumetric capacities and enabling greater energy densities in multivalent battery systems. Calcium-ion batteries (CIBs) have emerged as a particularly promising technology. Calcium is the fifth most abundant element in the Earth's crust, making it far more plentiful than sodium, magnesium, and approximately 2500 times more abundant than lithium. Its abundance ensures lower material costs for large-scale battery production. Additionally, calcium is nontoxic, posing minimal environmental hazards, which makes it suitable for sustainable energy storage applications.

Calcium also exhibits favorable electrochemical properties. Its deposition potential is only 0.17 V higher than lithium and 0.5 V lower than magnesium, enabling higher cell voltages and energy densities compared to magnesium-ion batteries. Despite being a heavier element, calcium, when measured by mass per electron transferred, is actually lighter than sodium, further enhancing its viability as a battery material. [68] Recent research highlights the feasibility of calcium-ion storage in 2D MXene materials. For instance, V_2CT_x MXene demonstrates a reversible specific calciation

capacity of 120 mAh/g at a current density of 50 mA/g. Electrochemical analysis confirms redox charge storage dynamics, with changes in vanadium oxidation states observed during calcium-ion insertion, supported by ex-situ X-ray photoelectron spectroscopy.[69] This investigation marks an important step toward utilizing 2D MXene materials for calcium-ion storage and underscores the potential of nano-confined fluid systems to improve charge storage capacities in multivalent electrolytes. Despite these advantages, rechargeable calcium metal batteries face challenges, particularly the irreversible nature of calcium metal anodes caused by the formation of non-ionically conductive solid electrolyte interphases. As an alternative, calcium-ion batteries require the development of charge storage materials that exhibit both reversibility and efficient diffusion of high-charge-density calcium ions. Addressing these challenges through materials innovation and electrolyte optimization could position calcium-ion batteries as a sustainable and high-performance solution for stationary energy storage applications.

In addition to zinc-ion batteries (ZIBs) and magnesium-ion batteries (MIBs), aluminum-ion batteries (AIBs) present a promising alternative to lithium-ion batteries (LIBs). Aluminum is abundantly available, comprising approximately 8.2% of the Earth's crust, making it a cost-effective and sustainable option. Furthermore, AIBs are environmentally friendly and offer a high theoretical capacity of 2980 mAh g^{-1}, positioning them as strong contenders for next-generation energy storage solutions.[70] Aluminum anodes, unlike lithium metal anodes in LIBs, exhibit minimal risk of dendrite formation due to the presence of a stable oxide layer and a higher standard reduction potential (−1.662 V vs. standard hydrogen electrode). Similar to MIBs, AIBs utilize organic or ionic liquid electrolytes, which can limit ion and electron migration. MXenes, with their large surface area and exceptional conductivity, offer a promising solution by facilitating efficient charge transfer and improving ion transport, making them well-suited for use in AIB systems.[71]

9. Prospects, Outlook, and Recommendation

MXenes have demonstrated remarkable potential as active materials for electrochemical energy storage, particularly in Zn, Mg, and Ca-ion batteries, as well as in a range of other applications. Despite significant advancements in recent years, several challenges remain that must be addressed to fully realize their potential. One pressing concern is the synthesis process, which commonly relies on hydrofluoric acid (HF). While effective, HF poses severe health and environmental hazards. Future research should focus on identifying safer alternatives to HF, such as fluoride-free or minimally hazardous etching techniques, that are cost-effective and environmentally sustainable. Developing scalable, eco-friendly synthesis methods is essential for enabling the large-scale production of high-quality MXenes suitable for industrial applications.

Another challenge lies in the electrochemical performance of MXenes. Their electrodes typically exhibit pseudocapacitive behavior with sloped discharge curves, leading to excellent rate performance but relatively low energy densities. While MXenes are highly conductive and ideal for high-power hybrid ion capacitors, their limited capacitance can be a drawback for high-energy storage applications. To overcome this limitation, researchers should explore compositional tuning and hybridization strategies, integrating MXenes with materials that offer higher specific capacities. This approach could significantly enhance their performance, making them viable for high-energy and high-power-density devices.

Moreover, MXene materials are highly sensitive to oxygen and moisture, leading to structural degradation and reduced stability. Addressing these issues requires advancements in surface passivation, coatings, and encapsulation techniques to improve stability without compromising performance. The development of protective layers and functionalized MXenes can mitigate oxidation and structural collapse, ensuring long-term durability in practical applications.

In conclusion, while MXenes offer exciting opportunities for energy storage, their widespread adoption depends on overcoming challenges related to synthesis, stability, and performance optimization. Continued research efforts focusing on safer fabrication methods, structural stabilization, and material hybridization will be critical for bridging the gap between laboratory research and commercial implementation. With these advancements, MXenes could emerge as leading materials for next-generation energy storage technologies, providing sustainable, high-performance solutions for diverse applications.

10. Conclusion

This review comprehensively analyzed the synthesis, structural properties, and electrochemical performance of MXenes, emphasizing their potential as active materials for divalent ion batteries. It highlighted MXene's superior conductivity, tunable chemistry, and layered architecture, which enable enhanced charge storage, stability, and scalability in electrochemical systems. Addressing the challenges of ion diffusion kinetics and structural degradation,

the study proposed strategies for optimizing MXene-based composites to improve energy density and cycling performance. By advancing the development of sustainable and high-performing energy storage solutions, this study paves the way for broader adoption of renewable energy technologies, ultimately contributing to a cleaner and more energy-efficient society.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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