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Recent Advance and Future Perspective of 2D MXene for Energy Storage: Mini Review

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Abstract: MXene is deemed to be one of the best attentive materials in an extensive range of applications due to its stupendous optical, electronic, thermal, and mechanical properties. Different MXene-based nanomaterials with extraordinary characteristics have been proposed, prepared, and practiced as a catalyst due to its two-dimensional (2D) structure, large specific surface area, facile decoration, and high adsorption capacity. Transition metal carbides and/or nitrides (MXenes), a developing class of 2D layer-structure compounds, are being given a lot of attention as one of the most promising classes of energy storage materials due to their numerous advantages, including high electrical conductivity, tunable layer structure, small band gap, and functionalized redox active surface. Bottom-up synthesis, which uses chemical vapor deposition, a template approach, and pulsed laser deposition with plasma enhancement, and top-down synthesis, which uses etching and exfoliation, are the two basic types of synthesis. In this review paper, more than 56 articles where reviewed on 2D MXene materials along with their application in energy storage battery. Numerous applications for energy storage exist for nanomaterials based on (2D) MXene. Even though 2D MXene could have some drawbacks, a lot of research has gone into nanoengineering these 2D materials to improve their functionality for real-world applications. Recent literature has described various uses for 2D MXene materials in lithium-ion batteries, sodium-ion batteries, lithium-sulfur batteries, and supercapacitors. To progress in facilitating their industrial application, the difficulty and prospective future are also examined.

Keywords: 2D Materials, Etching, Energy Storage, MXenes, Synthesis

1. Introduction

A decade of research on two-dimensional materials (2DMs), starting with graphene and moving on to 2D polymers, metal oxides, transition metal dichalcogenides, and other materials, has culminated in MXene, a novel material now under development.

$M_{n+1}X_nT_x$, where M is the transition metal, X is carbon and/or nitrogen, and T is a functional group like fluorine, hydroxyl, or oxygen, describes a type of two-dimensional transition metal carbides/nitrides with randomly dispersed functional groups on the surface [1]. Due to their 2D structure, nanosheets-like materials have unusually high specific surface areas, and the effect of quantum confinement in one primary direction may result in extraordinary physical and chemical capabilities [2], MXenes, a group of compounds made up of layers of transition metal carbides, nitrides, or carbonitrides that are only a few atoms thick (to emphasize their graphene-like form), have various characteristics that make them a promising new class of 2D materials.

They not only share many of the same intriguing properties as 2D materials, but also possess some even more desirable qualities, such as diverse chemical composition options, controllable surface chemistry, an unusual combination of metallic conductivity and hydrophilicity, and a number of intriguing electronic, magnetic, optical, and thermoelectric behaviors.

As a result of the aforementioned characteristics and the sharp growth in publications, the scientific community has recently become interested in MXene and other two-dimensional materials. The three primary MXene synthesis techniques are etching, top-down synthesis, and bottom-up synthesis. When meticulously creating the structure using the bottom-up synthesis manufacturing method, as opposed to the top-down fabrication strategy, which often requires a

significant number of precursor materials. The precursors can be put together in a specific 2D order to form the MXene structures using a crystal growth process. The benefits of the bottom-up strategy enable fine control of the size distribution, shape, and surface terminal functions of MXenes [3].

Although etching is the primary method for producing MXenes, other approaches have not succeeded in producing stable single- or few-layer MXene colloidal dispersions, possibly due to difficulties with intercalation, delamination, or colloidal stability during amalgamation [4], the A layers from the MAX phases [5]. which are ternary carbides or nitrides having the typical chemical formula $M_{n+1}AX_n$, where M represents an early transition metal, A represents a group IIIA or IVA element, X represents C and/or N, and n = 1, 2, 3 [6]. For instance, V_2C MXene samples were created by selectively etching V_2AlC at 90°C in two distinct environments: open (OE) in oil bath pans at atmospheric pressure and closed (CE) in hydrothermal reaction kettles at higher pressures [7], in aligned to this, by wet etching the parent MAX-phase in HF-containing solutions, MXenes are produced. Scaling is challenging due to the acute toxicity of HF, and surface composition and grafting process control are complicated by competing surface hydrolysis. Authors also describe an efficient anhydrous room-temperature etching method for producing MXenes from Ti_3AlC_2 utilizing halogens (Br_2, I_2, ICl, and IBr) [8]. However, research in this issue produced a general overview on the synthesis of 2D MXene materials by etching methods in good ways Missing may be stability of the nanomaterial and how we reduce the utilization of strong acid during synthesize.

MXenes have been extensively investigated for their potential uses in a variety of domains, including those involving in Li-ion batteries (LIBs), electrodes, supercapacitors, hydrogen storage, adsorption, and catalysts [9]. Overall, the majority of the described MXenes have characteristics that are attractive for electrochemical energy storage applications, including high electronic conductivity, mechanical property, and hydrophilicity [2].

With improved performance for energy storage applications such as lithium-ion batteries, sodium-ion batteries, lithium-sulfur batteries, and supercapacitors, the goal of this review is to provide a detailed description of the prior works in the field of nanoengineering of 2D MXenes and their derivatives. We also go over various synthesis techniques for 2D MXene materials, including the top-down and bottom-up approaches that are most frequently used. Finally, we talked about the shortcomings and potential of the 2D MXene materials for energy storage applications.

2. Synthesis Method of MXenes

Top down procedures, such as etching and exfoliation, are the two most used methods for creating 2D MXene materials. Additionally, bottom-up strategies such as chemical vapor deposition, a template technique, and pulsed laser deposition with plasma enhancement have been reported [10].

2.1. MXene Synthesis by Top-Down Methods

Using a top-down method, large volumes of crystal are exfoliated into single-layered MXene sheets [11]. Top-down MXene synthesis preserves the $M_{n+1}X_n$ layers while selectively removing the A atomic layer from the precursor [12].

2.1.1. Etching Approaches

The MAX phase has a three-dimensional (3D) structure before the etching process, and the etching process can transform the MAX phase into MXene, which has a two-dimensional (2D) layered structure [13]. Once the chemical bond between the M and A elements in the MAX phase is severed during the etching process, the A elements are removed. The strong M-X bond is a combination of covalent, metal, and ionic bonding, whereas the M-A link is metallic in nature. High temperatures have the ability to rupture the MX and MA connections, resulting in a structure resembling a rock. Additionally, when etching with particularly corrosive chlorine, both M and A elements are eliminated, which causes the creation of carbide derivatives. Therefore, the two etching methods should be carefully chosen, and the A element should be selectively removed using a suitable method. [14].

Many researchers have reported MXene Synthesis by Etching method. At a temperature of 90°C, ternary carbide V_2AlC was etched using three etching solutions. Lithium fluoride plus hydrochloric acid, sodium fluoride plus hydrochloric acid, and potassium fluoride plus hydrochloric acid made up the three solutions. It was discovered that the only solution proficient to producing very pure V_2C MXene was NaF + HCl [15]. In another study, MXene was Amalgamated by selective etching of silicon from layered MAX phase (Ti_3SiC_2) via etching solution consisting of HF and an oxidant (H_2O_2 or $(NH_4)_2S_2O_8$ or HNO_3 or $KMnO_4$ or $FeCl_3$) (Figure 1) [16]. In aligned to these, Ti_3AlC_2 precursor is produced using a low-cost technique that combines self-propagation high-temperature synthesis (SHS) and grinding. $Ti_3C_2T_x$ MXene is then produced using this precursor. For the SHS-ground precursor to completely etch A-layer and change the 3D structure into a 2D state, the same etching conditions as those for pressure-less synthesized precursors are necessary [17]. However, research on this subject resulted in a thorough examination of the methods for producing 2D MXene materials that use efficient etching. Numerous other safe etching agents should be extensively explored and addressed, as opposed to using dangerous and corrosive fluoride-containing acidic solutions during synthesis.

2.1.2. Exfoliation Approaches

Because interlayer distances have a fundamental impact on a variety of applications, including electrochemical performance in 2D materials, research has focused on lowering interlayer Van der Waals bonds to improve MXenes exfoliation [18]. For instance, [19] reported about the synthesis of the 2D MXene Ti_3C_2 by exfoliating the MAX

phases with bi fluoride salt. This method have many advantage like that of, Less aggressive reactants than HF; less time spent sonicating (at least four times); higher

exfoliation yield, with 70% of the flakes having one or two layers; reduced vacancies; and a clay-like MXene that is extremely malleable and pliable [20].
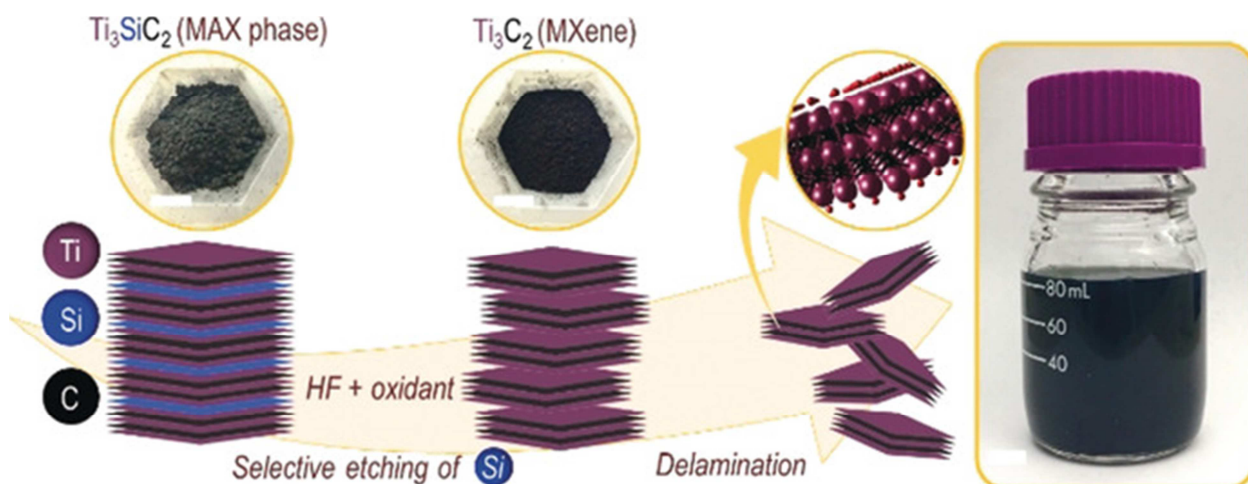

Figure 1. *Synthesis of MXene was achieved through selective etching of silicon from layered MAX phase (Ti$_3$SiC$_2$) using etching solution (16).*

2.2. MXene Synthesis by Bottom up Methods

Many bottom-up synthesis methods have also been developed as a result of recent developments, including the template approach, plasma enhanced pulsed laser deposition, and chemical vapor deposition (CVD) (PEPLD). In contrast to selective etching, materials produced by bottom-up techniques, particularly CVD, exhibit better crystalline quality. Furthermore, these methods enable the synthesis of 2D transition metal carbides (TMCs) and nitrides (TMNs), including heterostructures, WC, TaN, and MoN, with stoichiometries that are not possible to achieve through selective etching. It is important to understand that employing these approaches, thin films with many layers rather than single layers of TMCs or TMNs have been formed. The thin films, however, exhibit 2D properties, for instance in superconducting transitions [10].

2.2.1. Chemical Vapor Deposition (CVD) Methods

The synthesis of MXenes can also be carried out via

bottom-up synthesis techniques like CVD [21]. CVD has been widely employed in producing high-quality and large-area materials which is an effective tool in applications such as integrated electronic devices and flexible optoelectronics [22]. Abundant 2D materials including graphene and TMDs have been fabricated by CVD. Typically, the substrate and raw materials are placed in a reaction chamber, and large-scale ultrathin 2D materials will be obtained under appropriate conditions. In 2015, Xu et al. synthesized ultrathin Mo$_2$C crystal by CVD. Due to high growth temperature, the Mo$_2$C crystals produced by copper-catalyzed CVD were orthorhombic (α-Mo$_2$C). The lateral size and thickness of α-Mo$_2$C changed with experimental conditions (e.g. growth temperature and time [23].

In order to create N-doped Ti$_3$C$_2$T$_x$ MXenes/P composite with a walnut-like structure for the first time and demonstrate their viability as anode materials for LIBs, Zhang et al., 2019 developed a chemical vapour deposition process. Figure 2. Depict the thorough manufacturing process for N- Ti$_3$C$_2$T$_x$ MXenes/P.
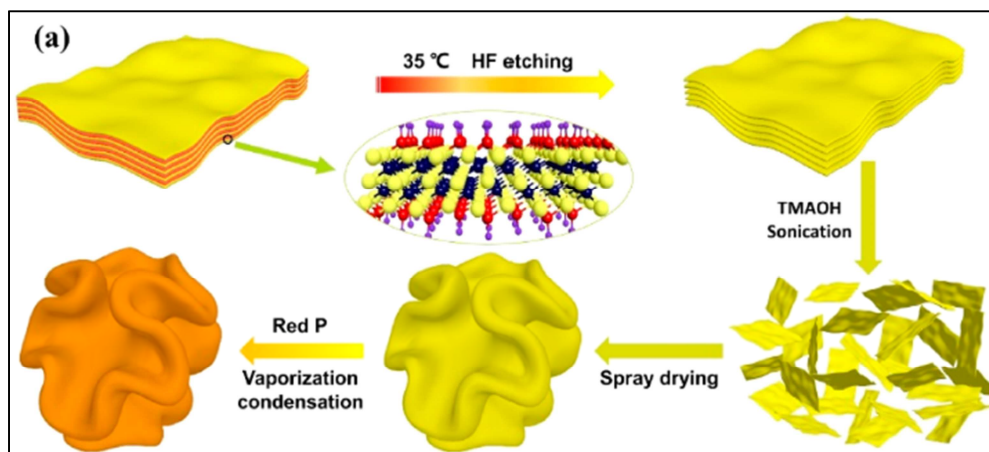

Figure 2. *(a) Schematic illustration of the preparation process of N-doped Ti$_3$C$_2$T$_x$ MXenes/P composites (N−Ti$_3$C$_2$T$_x$/P) (24).*

The Ti_3C_2Tx MXenes' walnut-like structure matrix gives the composites high conductivity, prevents red P particles from aggregating, and gives room and flexibility to increase capacity during cycle. Red P particles contribute to large reversible capacity under the premise of improving composite conductivity by Ti_3C_2Tx MXenes, showing obvious improvement of electrochemical performance in the MXenes field yet. Additionally, to the best of their knowledge, those was the first attempt to focus on vapor deposition of red P into an MXenes matrix to prepare composites, which can be applied as electrodes for high performance LIBs with superior rate performances. The outstanding advantage of this facile method is that the preparation method is universal and reproducible. A series of MXenes and P composites work can be put forward and optimized via different structural MXenes matrixes and subsequent vapor deposition of red P [24]. In general, chemical vapor deposition (CVD) produces high-quality films on various substrates. This approach is not generally used to make MXenes, because the films obtained are not single layer, but rather very thin films.

2.2.2. Template Methods for the Synthesis of 2D

In addition to CVD, template methods have also been advanced for synthesizing 2D MXenes [25]. Matched to CVD methods, the template method has much higher yields. All the template methods use 2D transition metal oxides (TMOs) Nano sheets as templates, and these TMOs Nano sheets were subsequently carbonized, or nitride to synthesize 2D MXenes. describe template methods as a scalable approach for producing 2D nitrides like MoN by reducing 2D hexagonal oxides in ammonia. A great deal of research has been done on MoN nanosheets of sub nanometer thickness. Experiments and theoretical calculations both show that 2D MoN is metallic. The hydrophilic restacked 2D MoN sheet demonstrates an exceptional rate performance and a very high volumetric capacitance of 928 Fcm_3 [25].

2.2.3. PEPLD Synthesis Methods

A PEPLD technique has recently been devised to create large-area, ultrathin FCC Mo_2C films on sapphire. This method combines the benefits of pulsed laser deposition and plasma assisted chemical vapor deposition. In this synthesis, a high-quality Mo_2C layer was deposited on a sapphire substrate by heating it to 700°C while employing CH_4 plasma as a C source to react with the Mo vapor produced by the pulsed laser. They discovered that Mo_2C is more likely to develop in CH_4 plasma. The resulting films had significantly worse crystalline quality than the CVD-grown samples, and cross sectional TEM images show numerous stacking defects [26].

3. Energy Storage Application of 2D MXene

2D MXene materials are highly conductive and have high specific surface area, which is beneficial for several potential applications in energy storage and conversion [27]. 2D MXene also have many similar modification methods to tune morphology, crystalline structure and surface properties for specific applications. Typically, the porosity and curvature of MXene can be adjusted to produce more specific surface area and pore volumes. Furthermore, the microstructure of MXene materials can be also modified with heteroatoms (metal or non-metal) doping and surface modifications to achieve higher performance. This similarity provides promising perspectives of MXene based materials for energy storage and conversion applications [28].

Nowadays, 2D MXene materials, which possess substantial chemical and structural variety, have been explored as promising stars in various applications including energy storage [28], hydrogen evolution reactions [29], oxygen evolution reactions (OER) [30], water purification [31], CO_2 sensor [32] electromagnetic interference [33] and soon. In this Review, the latest research and progress on 2D MXene-based nanostructures are introduced and discussed, focusing on their applications for energy storage such as lithium-ion batteries, sodium-ion batteries, lithium-sulfur batteries and supercapacitors.

3.1. 2D MXene for Lithium-Ion Batteries

Two-dimensional MXene is a promising anode candidate for lithium ion battery. Rechargeable lithium-ion batteries have occupied the power source for laptop computers, mobile phones, digital cameras and videos, because of their enhanced energy densities, which are 2 to 3 times the energy per unit weight and volume compared to conventional rechargeable batteries [2]. The fast rate of charge or discharge process in rechargeable lithium-ion batteries can deteriorate the electrochemical characteristics of lithium-ion batteries.

To improve the electrochemical performance of rechargeable lithium batteries, it is crucial to create novel materials or technologies.

Due to their numerous chemical and structural variations, 2D MXene are competitive with other 2D materials for high power lithium-ion battery applications [34].

Formula weights of 2D MXenes materials play a part in energy storehouse operation. It was set up that MXenes with low formula weights, like V_2C, Ti_2C, Sc_2C and Nb_2C, are the most promising candidates due to their high theoretical gravimetric capacities [35]. Because a very strong bonds between M and X, it is assumed that metal ions only diffuse between the MXene sheets. Because Ti_3C_2 has one inactive TiC layer, Ti_2C have higher gravimetric capacitance than that of Ti_3C_2. This was also experimentally verified and handed evidence that the specific capacity of Ti_2CT_x for Li-ion uptake is much higher than that of $Ti_3C_2T_x$ attained in the same method [36]. Also, Li-ion storage capacity is highly depending on the surface functional groups. Tang et al., 2012 reported that, the calculated Li diffusion barriers suggest high lithium ion mobilities in oxygen terminated MXenes owing to their favor to lithium ion transport, whereas, the Li-ion

storage in OH terminated MXenes show that inadequate capacity [37].

3.2. 2D MXene for Sodium-Ion Batteries

During the past decades, tremendous efforts have been made to develop attractive rechargeable battery systems for portable electronic devices and electric vehicles because of growing cost and limited lithium sources in nature. Nowadays, sodium-ion batteries (SIBs) represent the promising systems for large-scale energy storage owing to the abundance and low cost of sodium [38]. The performance of electrochemical energy storage (EES) devices highly relies on the in-built properties of the material. Because of the excellent properties of 2D materials, a much of research has been conducted on 2D materials. In the past decade, a novel family of 2D carbides and nitrides materials has been successfully prepared called MXene using stripping method, from layered precursors. Because of the abundant sodium resources in the earth's crust and wide distribution in the world, sodium ion batteries have great potential for large-scale application. Therefore, sodium ion battery can be used as an important complementary technology of lithium-ion battery in the field of large-scale energy storage, which has important economic value and strategic significance. Sodium-ion batteries have suitable redox potential (E^0 Na^+/Na = 2.71 V vs SHE) and similar energy density to lithium ion batteries. Sodium-ion batteries become an ideal electrochemical energy storage device to replace lithium ion batteries [39].

The may importance of sodium ion battery, few of them are as follows: abundant sodium resources, uniform distribution and low cost; the working principle of sodium ion battery is similar to that of lithium-ion battery, which is compatible with most of the production equipment of lithium- ion battery; since aluminium and sodium do not undergo alloying reaction at low potential, cheap aluminium can be used for the collector of both positive and negative electrodes of sodium ion battery; in solid-state batteries, bipolar electrodes can be designed, and positive and negative materials can be coated on both sides of the same aluminium foil, so as to achieve higher voltage in a single cell and save other non-active materials to improve the bulk energy density; the solvation energy of sodium ion is lower than that of lithium ion, that is, it has better interfacial ion diffusion ability; the Stokes diameter of sodium ion is smaller than that of lithium ion, and the electrolyte with the same concentration has higher ionic conductivity than that of lithium salt electrolyte, the high and low temperature performance of sodium ion battery is better; no fire phenomenon is found in all safety project tests, Better security performance. The internal resistance of sodium ion battery is slightly higher than that of lithium ion battery, which leads to less instantaneous heat and lower temperature rise in safety tests such as short circuit, which is one of the reasons for good safety performance. More unique advantages of sodium ion battery will be gradually revealed with the deepening of the research. Mining these unique advantages will improve the differentiation of sodium ion battery products and make it occupy a favourable position in the future market competition [39–42].

3.3. 2D MXene for Lithium-Sulfur Batteries

Lithium-sulfur (Li-S) batteries (LSBs) have recently drawn a lot of attention because of their theoretically higher specific capacity and energy density than lithium-ion batteries [43, 44]. Although the average voltage plateaus of lithium-sulfur batteries lie at a lower value (2.2 V vs. Li^+/Li) compared with other cathode materials, the sulfur electrode can deliver a high theoretical capacity of 1672 mAh/g and an excellent energy density of 2567 Wh/kg based on the formation of Li_2S product, which are about 5-10 times higher than conventional cathodes for lithium-ion batteries [45]. Lithium-sulfur batteries also have many importance's, including low cost, abundance of sulfur, wide operating temperature range and prolonged cycle life. Liang et al., 2015 shows that 70 wt% S/Ti_2C composites exhibitstable long-term cycling performance because of strong interaction of the polysulfide species with the surface Ti atoms, demonstrated by X-ray photoelectron spectroscopy studies. The cathodes show excellent cycling performance with specific capacity close to 1200 mAhg¢1 at a five-hour charge/discharge (C/5) current rate. Capacity retention of 80%isachieved over 400 cycles at atwo-hour charge/discharge (C/2) current rate [46].

In addition lithium-sulfur batteries have been extensively investigated for several decades; the practical application of lithium-sulfur battery systems has been hindered by several drawbacks, namely, the low conductivity of sulfur and poor cyclability caused by the "shuttle effect". The general solution to overcome the above-mentioned issues is trapping sulfur species in a conductive carbon matrix. Thus conductivity of sulfur/carbon cathodes can be effectively increased and the dissolution of polysulfides in organic electrolyte can be decreased. Also computational calculations have been applied to investigated the anchoring effect of lithium polysulfides on various 2D materials [47].

3.4. 2D MXene for Supercapacitors

Supercapacitors have concerned great attention due to their high-power density than conventional batteries [48]. Thus, supercapacitors are considered as the best candidates for next generation high power systems. There are two typical categories of storage mechanisms for supercapacitors. The first one is electrical double layer capacitor (EDLC), where the charges are stored in Helmholtz double layer near the surfaces of the electrode materials. In an ideal EDLC, the supercapacitor presents a classic rectangular cyclic voltammograms without any redox reaction, resulting in outstanding power performance [49]. Due to the charges are reserved on the surface of electrode materials, the specific energy density of supercapacitors is limited.

To ensure quick electron transit, MXenes with high metallic conductivity are frequently investigated for use in supercapacitor application, with the first found MXene, $Ti_3C_2T_x$, remains the most conductive [50]. It has been

demonstrated that the 2D MXenes can be intercalated by metal ions suggests that the MXene possesses the capacity to store charge. Example of cations that can electrochemically intercalate MXenes include Li^+, Na^+, K^+, NH_4^+, Cs^+, TEA^+ and Mg^{2+}, Ca^{2+} and Al^{3+}. These cations occupy electrochemically active site on the MXenes surface and held with energy storage [51]. In MXenes, ion adsorption sites cover the shallow adsorption sites and deep adsorption sites. Ions are always accommodated on shallow adsorption sites near the edges of particles firstly and then on deep-adsorption sites in the particle's interior with higher activation energy for ion adsorption. Therefore, at high scan rates, the ion can be adsorbed on the shallowadsorptionsites in afast mannerto guarantee acertainamount of charge storage, which made MXene exhibit excellent rate performance. Additionally, cation intercalation is accompanied by the change of confined water between interlayers. Typical cosmotropic cations (Li^+, Mg^{2+} and Al^{3+}) are intercalated into the MXene interlayers in their partially hydrated form without dehydration, whereas insertion of chaotropic cations (Cs^+ and TEA^+) effectively dehydrates the MXene. 120 During cycling, the ion insertion–extraction process in aqueous electrolytes always leads to changes in the c values. Unlike the interlayer space expansion in carbon materials, different ions result in different deformation behaviours in MXenes. In general, cations with smaller ionic radii and higher charges contract the void of $Ti_3C_2T_x$ MXene, while larger cations with smaller charges expand the interlayer spaces, which imply that there exist a confrontation between the expansion owing to the cation intercalation and an electrostatic attraction between the negatively charged $Ti_3C_2T_x$ sheets with positively charged cations between the sheets. Finally, if contraction dominates over expansion, the interlayer distance will increase; otherwise, the interlayer space will contract [52]. The gravimetric to volumetric capacitances in solid state supercapacitors can be greatly enhanced by the use of MXene-based electrode materials, making them potentially attractive for high power transportation energy systems.

New supercapacitor systems with higher power and energy densities can yet be developed, though. For instance, controlling porosity is a simpler way to increase surface area and hence enhance EDLC than changing the curvature of 2D MXene. Consequently, innovative research and development are essential to obtaining new materials and technologies for high-performance supercapacitors [2].

4. Conclusions and Future Perspectives

The most current developments in research on 2D MXene materials for energy storage applications, such as lithium-ion, sodium-ion, lithium-sulfur, and supercapacitor batteries, are summarized in this study.

Despite extensive research being done on these 2D materials over the past few decades, a number of barriers still stand in the way of their actual usage.

The key issue from the point of view of materials synthesis is to make 2D materials as thin as feasible by using effective exfoliation techniques. The specific surface area and reactivity of 2D MXenes materials will obviously grow with decreasing thickness dimension. It is well known that MXenes' surface functional groups significantly affect how well they operate electrochemically. However, increasing the number of active sites also depends on morphological change. There are also many other challenges to overcome in the creation of materials based on MXene. The MXene family needs to be widened in order to produce additional Mn+1XnTx with different metals (M) and functions of T and x.

It will be advantageous to regulate and modify their surfaces in order to create MXenes with the necessary properties.

For instance, reduced conductivity may be the result of MXenes with surface functional groups. MXenes without functional groups can be created with excellent electrochemical performance. Additionally difficult is the preparation of single-layered MXene on a large scale. A wide range of applications for MXene-based materials will be possible if the aforementioned issues can be resolved. By developing novel techniques and methods for producing 2D MXene materials that have excellent chemical stability and endurance, the performance of the manufactured devices should be enhanced.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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