A Review on MXene: Synthesis, Properties and Applications on Alkali Metal Ion Batteries

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Abstract. As a new type of two-dimensional material, MXene has been extensively known due to its various functional groups. The profuse surface terminated functional groups bring good conductivity and hydrophilicity to MXene, make it a good material for batteries. In this article, the synthesis, properties and batteries applications of MXenes were introduced, and the current challenges and outlook for future research on MXene applications was discussed.

1. Introduction

With the increasing demand for recyclable energy in every country, people have made many efforts to develop new materials for high-efficiency metal ion batteries. In recent years, lithium ion batteries (LIBs) have become the equipment which most commonly used to store energy in chemical way. Due to the shortage of lithium resources and uneven distribution, the development of lithium-ion batteries is restricted. Alkali metal ion batteries represented by resource-rich and low-cost sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs) have also caused widespread popularity attention. Based on the working principle of electrochemical energy conversion and storage, the surface and interface make a key role in ion intercalation, physical/chemical adsorption and electrochemical reaction processes [1]. Two-dimensional materials with a broad specific surface area and high electrical conductivity represented by graphene, transition metal disulfides, transition metal oxides, hexagonal boron nitride, silylene, phosphorene, etc., are considered to be the most recent decades. The preferred material for chemical energy conversion and storage [2-3]. For reusable metal ion batteries together with electrochemical energy conversion applications, two-dimensional materials have the following advantages:

a. The crystallized inner structure provides a cover with low cost for the rapid electrons to transport into the layers in atom level.

b. The layered inner structure produces many different paths for metal ions to diffuse, becomes a beneficial way to the diffusion of metal ions

c. The two-dimensional structure offers a elasticity space to cover the change of volume when the electrochemical reaction take place, keeps a excellent contact from one layer to another [3-5].

In addition to this group of 2D materials, a new two-dimensional metal carbide and/or nitride (MXenes) with special surface electrochemical performance, adjustable structure and physical and chemical properties have attracted more and more attention when applied in the energy conversion and storage area.
Since the first report of Ti$_3$C$_2$Tx MXene in 2011, this new material produced by selective etching of MAX phases represents a promising electrode material in supercapacitors [6]. Due to its unique oxygen/fluorine functionalized surface, MXenes has huge application potential in lithium/sodium/potassium/magnesium/aluminum ion batteries [7-12]. However, most recent researches only focused on the properties of MXenes, but only a few paid attention to the surface modification of MXene (said as "naked MXenes"). Surface modification of MXenes materials and construction of composite materials are required to solve the above-mentioned development of high-performance storage problems in energy technology.

This article briefly summarizes the preparation methods of MXenes discovered so far, and explains the challenges and prospects of MXenes nanocomposites in the application of alkali metal ion batteries.

2. Synthesis of MXenes

2.1. The structure of MXenes

Generally, MXenes refers to the extraction of MnXn-1 (n=2,3,4) layers from the metal-ceramic MAX phase by removing interlayer A atoms (MAX, where M=early transition metal; A=IIIA or IVA group elements; X = C, N) [13]. As shown in Figure 1, the M and X atoms in the MAX phase are stacked into a hexagonal lattice, and the X atoms occupy the center of the M octahedral cage shared by the edges. After removing the A atoms, the MnXn-1 layer can still maintain the hexagonal lattice instead of the cubic structure of MX, so the MnXn-1 layer can be obtained by extracting the A atoms. MXenes thin films are usually arranged horizontally, which is inherited from the predecessor MAX. Most MXenes show high mechanical properties, and these materials are expected to be used in nano-devices with mechanical requirements.

![Figure 1. selective “A” layer etching [14]](image-url)
2.2. MXenes preparation method

There are many ways to prepare MXenes. Due to the difference in the etching process, different end groups can be bonded with M atoms to complete their coordination spheres to minimize the surface Gibbs free energy (Gsurf). So, the surface characteristics of MXenes layers lead to a large extent on the preparation method. The preparation methods are now classified as follows.

2.2.1. Hydrofluoric acid (HF) etching method. With people’s in-depth research on MXenes, more and more etching methods have been applied to scientific research, and the most traditional etching method is still the HF etching method. The HF etching was first proposed by Naguib et al. [15] in 2011, with the purpose of stratifying the Ti3AlC2MAX phase. Hydrofluoric acid could remove Al layers straight forward from Ti3AlC2 MAX phase by an easy displacement reaction, which produces H2. Also, the deionized water and hydrofluoric acid solution will also take reaction which produced Ti3C2 to achieve Ti3C2Tx (T = -OH, -F or -O) while produce H2 as well. Successfully include Ti2AlC, Ta4AlC3, (Ti0.5Nb0.5) 2AlC, (V0.5Cr0.5) 3AlC2, Ti3AICN, Nb2AlC, by HF etching method, a series of MAX compounds of Ti3SiC2, Mo2GaC and Zr3Al3C5 were stripped into MXenes [16-20].

From 2011 to 2020, the hydrofluoric acid etching keeps becoming the most commonly used MXenes material synthesis method. The temperature, time, and the F ion density of the etching process play unique roles during the formation of good quality MXenes layers. However, stronger acid etching may lead to greater surface defects and may decrease the output quantity of MXenes [21]. It was confirmed by Alhabeb et al. [22] that Ti3C2TX produced by high concentration hydrofluoric acid will provide a good layered shape, while it is difficult to obtain by using different acid solutions.

By using the hydrofluoric acid etching method, the produced MXenes showed their original surface features, with -(F), -(OH) and =0 functional groups.

2.2.2. Modified acid etching method. Due to the corrosive and toxic properties of acidic solutions containing fluoride, researchers have tried to explore different ways to prevent the direct etching of hydrofluoric acid to extract aluminum layers away from the MAX phases. The first method is an improved hydrofluoric acid etching method, which is called original place hydrofluoric acid etching method, while the hydrofluoric acid is substituted with a combination of fluoride salt (NH4HF2, LiF, NaF, KF and FeF3) and HCl [23-24]. The interlayer distance of the MXenes obtained by the modified acid etching method is increased due to the intercalation of cations, which reduces the inner force from on layer to another, and it is beneficial to delaminate material layers during the ultrasonic process. Therefore, this method simplifies the cumbersome multi-step synthesis process described above, and realizes the possibility of synthesizing a few-layer MXenes in one step [23].

2.2.3. Molten fluoride salt etching method. In addition to the common carbide MXenes, nitride MXenes is also an important part of the MXenes family. TiNn-1 is more stable than TiNn-1. In the TiNAlNn-1 system, the bonding of Al atoms is stronger. During the etching process, TiNn-1 could be etched by the hydrofluoric acid solution.

In order to overcome the above-mentioned challenges, Urbankowski et al. [25] introduced a ternary eutectic molten fluoride salt (LiF: NaF: KF = 29: 12: 59, weight ratio) as an etchant for the synthesis of Ti4N3Tx MXene. Comparing to different hydrofluoric acid etching produced titanium-carbide MXenes (such as Ti3C2Tx), the layered Ti4N3Tx has a poorer crystallinity. Therefore, it residues many complicated problems during the synthesis process to produce 2D metal nitride by the molten fluoride salt etching method. Therefore, the hydrofluoric acid etching chemical process is stays the best way for the production of MXenes.

2.2.4. Non-fluorine etching method. Since acidic solutions containing fluoride are corrosive and toxic, many other safe and economical etching reagents is extensively researched. In 2018, Yang et al. [26] demonstrated a synthesis way without fluorine ions for Ti3C2 layering in a binary water electrolyte, which achieved high yields of Ti3C2Tx nanosheets. Due to the large chemical forces between Cl- and
aluminum ions, the mixed solution composed of 1.0M ammonium chloride (NH4Cl) and 0.2M TMAOH (pH value> 9) was selected as the electrolyte. In the production process, the aluminum atoms are etched by Cl ions when the insertion of NH4+ ions occurs. Due to the exclusion of F, the stripped Ti3C2Tx (T=O, OH) sheet has no fluorine groups and exhibits a significant are-specific capacitance in the application of supercapacitors.

In addition to acid etching, a more economical method is to use high-temperature, high-concentration alkaline solution (NaOH) to dissolve the A layer in the MAX [27]. The method is also fluorine-free, and can obtain up to 92% (quality score) of multi-layer Ti3C2Tx (T = O, OH). Generally, the Ti3C2 framework is unstable under alkaline conditions, and the corrosion of the Ti3C2 framework will occur at the same time with the etching of aluminum layers. So, maintaining the integrity of the Ti3C2 layer while selectively etching the A atoms from Ti3AlC2 remains a challenge. Application of high temperature (270 ℃), high alkaline concentrate (27.5M) conditions to prevent damage to the Ti3C2 framework; high alkali concentration and less water content could keep the oxidation from titanium layers. Through these fluorine-free etching methods, the surface of the Ti3C2 layer is filled by -OH and =O groups.

But in the same time, the high concentration NaOH solution presented before requires thermal energy from heat, potential energy from pressure force and hydrothermal conditions, leading to certain safety problems. So, Xuan et al. [28] took place new medium organic alkali etching method suitable for Ti3AlC2 layering, the tetramethylammonium hydroxide (TMAOH) was selected as the etching agent.

2.2.5. Other etching methods. In addition to traditional etching processes and improved etching methods, non-etching methods have also developed greatly in recent years. Xu et al. [29] prepared ultra-thin α-Mo2C MXene through chemical vapor deposition (CVD) strategy, which has the characteristics of large area and clean surface. Although a large number of studies have shown that the CVD method and the pyrolysis method have successfully synthesized MXenes, the structure of MXenes carbides/nitrides still needs careful identification.

In addition, the comparing above synthesis methods shows the different structures of the surface functional groups form one method to another. In addition to common etching methods, MXenes can be obtained through a variety of wet etching and subsequent stripping techniques [15-19].

3. Application of MXenes in alkaline metal ion batteries

As mentioned earlier, the stability, electronic structure and other physical and chemical properties of MXenes are greatly affected by its surface functional groups and structure. When used as an alkali metal ion battery, the thermal movement and molecular dynamics of the interlayer ion insertion and outspread of MXenes have aroused great interest. Through theoretical calculations and experimental research, there are still different views on the storage mechanism of different metal layers and various functional groups embedded in the surface of MXenes. Theoretical calculations show that, the difference in the surface functional groups of 2D metal carbides and nitrides and the types of different d and ds area ions influences the voltage and specific capacity of MXenes straight forward. The 2D materials with oxygen functional groups have the largest specific capacity, but the removal of -OH functional groups will result in a decrease in the specific capacity of MXenes. As well as the functional groups, the application of alkali metal batteries is affected by the number of layers stacked together inside MXenes. Single-chip or several-chips structures produces good conductivity to MXene and fully used the specific surface area of MXene layers to improve the ion transmission, helps electrolyte to infiltrate better, and when compounding with other materials, which contributes the inner layered structure occurs, compound to increase the specific capacity and increase the energy density.

3.1. Lithium-ion Battery

The key features of ion intercalation behavior have been reported theoretically and confirmed by experiments. Since the advent of MXenes, Tang et al. have taken the lead in using first-principles to predict the application potential of such materials in lithium-ion batteries. Calculations show that the
diffusion barrier of Ti3C2 without functional groups is 0.07 eV, and the theoretical lithium storage capacity is 320 mAh·g⁻¹, can be compared with commercial graphite anodes (372mAh·g⁻¹). But when Ti3C2 is completely fluorinated and hydroxylated, its theoretical capacity quickly drops to 130 mAh·g⁻¹ and 67 mAh·g⁻¹. Later, Xie et al. [10] proposed that compared with other surface groups, MXenes with =O end groups have the strongest lithium storage capacity, because the excess Li layer can be adsorbed on the MXenes that have been lithiated.

The electrochemical performance of MXenes composite material is significantly better than that of pure MXenes, and it shows fast and stable lithium storage performance. Due to the high conductivity of MXenes, MXenes composites can achieve the communication of metal ions on the surface, prevent the aggregation of active nanostructures during the embedding/extraction process.

3.2. Sodium-ion Battery
As sodium ion resources are abundant, widely distributed, and easy to obtain, people are paying more and more attention to sodium ion batteries (SIBs). However, the radius of Na⁺ is 1.4 times that of Li⁺, which creates a big problem when creating rechargeable anodes. Graphene is not able to be used in sodium ion batteries because of its low Na⁺ insertion/extraction rate, also the battery using graphene could not be recharged. At the same time, those elements can be combined with lithium ions in an easy way are also proved to be failed when combining with sodium ions.

The 2D MXenes materials present wide 2D ion moving paths and a large specific surface area, giving great quantity active sites for sodium ions to embed. Yamada et al. determined how to store the sodium ions inside 2D layered materials in non-aqueous electrolytes through nuclear magnetic resonance and density functional theory. Na⁺ is mainly intercalated between MXenes nanosheets. The interlayer spacing rised from 0.97 nm to 1.25 nm. Then, some of the Na⁺ ions will stay between the layers as "support pillars" to keep the enlarged interlayer space of MXenes, so that Na⁺ can be embedded/de-embedded and maintain MXenes’ good cycle stability in the sodium ion battery. The theoretical sodium storage capacity of Ti3C2 is 351.8 mAh·g⁻¹. However, the diffusion barrier of Na with a large ionic radius on bare Ti3C2 is about 0.20 eV, a bit smaller than lithium, result to slow electrochemical kinetics.

Therefore, it is a challenging opportunity to develop a suitable MXenes composite material electrode to replace LIBs with SIBs, especially in large-scale electric tools.

4. Conclusions
This paper introduces the latest research progress of 2D MXenes materials, expounds the synthesis methods of MXenes, analyzes the difference and similarity between the surface functional groups and the synthesis conditions under the four peeling methods, and summarizes the research progress of the preparation methods of MXenes in recent years. The application of MXenes-based nanocomposite materials in alkali metal ion batteries is discussed. Although these two-dimensional materials have been extensively studied in the past few decades, there are still many obstacles and challenges in the practical application of MXenes nanocomposites.

The development of MXenes nanocomposite materials requires the expansion of the MXenes family to discover more Mn⁺1XnTX with different functions. Regulating the surface function group of MXenes will be conducive to obtaining MXenes with the required attributes. Surface functional groups are the main factor affecting the electrochemical performance of MXenes, and the active sites can be increased through morphological modification. Different energy storage devices have different performance requirements for MXenes nanocomposites, such as: the type of functional group, the size of the specific surface area, and the porosity have different requirements. Successfully solving the above problems will be the key to expand the application of materials based on MXenes.

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