Development of 2D MXene for Energy Storage

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Abstract. The recently discovered large-scale two-dimensional (2D) early transition metal carbides and carbonitrides have captured people's attention as hot topics, called MXenes. MXene is a two-dimensional layered solid, linked by strong metals, ions and covalent bonds, e.g. Ti$_2$AlC, Ti$_3$AlC$_2$ and Ta$_4$AlC$_3$, usually by selectively etching the A element from the MAX phase to produce MXene. MXene has a an array of applications in all aspects cause its outstanding electrical conductivity, excellent specific surface area, good hydrophilicity and stability. In this article, the experimental and theoretical developments are reviewed in their synthesis, physicochemical properties and potential applications. MXene is expected to be applied in electrochemical energy storage and also provides current applications in batteries and super capacitor.

1. Introduction

On account of the continuous increase in energy consumption and the depletion of non-renewable resources such as fossil fuels, the demand for sustainable energy has greatly increased. In the past few decades, renewable energy has been extensively studied and applied. For example, solar, wind, hydroelectric and tidal energy have been developed to alleviate energy shortages and environmental risks. At the same time, from the perspective of sustainable development, electrochemical energy storage devices are dimed necessary to effectively store the energy of these renewable resources as to meet the needs of future developments[1].

As the one of the most extensively used energy storage device, the mechanism of the battery is electrochemical, that is mediated by an oxidation-reduction reaction. Batteries currently have high energy density, but low power density hinders their application in areas that require high power. On the contrary, the most common form of supercapacitor (SC) is to store energy by absorbing various ions in the electrolyte between layers to become an electric double layer (EDL) structure. The principle of the energy storage process is not based on chemical reactions, so because it is not controlled by chemical kinetics, the service life can be extended. On the other hand, SCs have fast charge/discharge capabilities, high power density and outstanding cycle stability, but the capacitance of SCs is a great deal of dependent on the electrode material and its potentially high specific surface area[2]. Their poor energy density cannot meet the ever-increasing energy demand such as the ever-increasing range demand for the Electric Vehicles. Note that the traditional electric double-layer capacitor (EDLC) achieves the purpose of storing charge through the physical ion adsorption/electrical permittivity process. The pseudo-capacitance material is a potential substitute for the double-layer capacitor material, and its principle is fundamentally that of the battery, namely a rapid surface redox reaction that can store more charge[3]. However, most of the general pseudo-capacitive oxides exhibit shortcomings such as poor...
electronic conductivity and poor structural stability, which is not conducive to their practical application in energy storage stability[4]. These energy storage devices complement each other and jointly promote the development of the energy storage field.

The MXene has attracted much attention recently because of its outstanding properties such as excellent surface area, adjustable electronic properties and extraordinary mechanical strength. Its low resistance and large interface area make it an ideal supercapacitor material. In this article, I will present a systematic study of these type of materials in the field of charge storage devices, in particular that of pseudo capacitors (redox capacitors).

2. Synthesis

In general, MXenes is a MAX-based 2D material with atomic layer thickness, where M stands for transition metals, A stands for 13-16 elements in the periodic table, e.g. Al, Si, Ge, Ga, etc., and X stands for carbon, nitrogen or their mixtures. In MAX, the MX bond shows the mixed characteristics of ionic/metal/covalent bonds, while the MA bond shows the physico-chemical characteristics of metal[5].

![Figure 1. Structure of MAX phases and their derivative MXenes][6].

MXene has different characteristics compared to their precursors. For example, for most MXenes, the electrochemical properties (such as mobility) decrease as the thickness increases, (a MXene flake is highly anisotropic, not unlike another layered material, graphite) which may be due to the increased layer barrier that makes it difficult for charges to transport. This is the main reason why we want to generate MXene instead of using MAX directly. For MXene, their stoichiometry can be expressed as $M_{n+1}X_nT_x$ (n is between 1 and 3), and T describe as a termination group (e.g. –OH, –O, –F)[6]. Since the $M-A$ bond shows the metal bond properties, it is very difficult to separate the $M_{n+1}X_n$ layer, and the manufacture of MXene always requires mechanical shearing of the MAX phase to achieve a thin layer. Although the $M-X$ bond is difficult to separate, the M-A bond have higher chemically active compared to the M-X bond, so that lead the pernickety etching of the A layer a new method, as shown in Figure 1. The key for fabricating MXenes is selective etching conditions[7].

So far, in order to develop new MXene and its derivatives, the development of new synthetic methods has become an important requirement. These methods can generally be segmented into two categories: one is the top-down method from the MAX phase precursor to MXene, the other is the
bottom-up strategy directly form the MXene film. Different synthesis conditions will synthesize different MXene morphology and surface termination characteristics, which will affect its properties, in particular for devices.

2.1. From top to bottom

2.1.1. HF etching

Figure 2 shows the schematic of the process. Hydrofluoric acid (HF) aqueous solution has become the most extensive choice for selective etching of MAX phase to synthesize MXene. When the element A layer is etched, the remaining part has the general formula $M_{n+1}X_nT_x$, with a surface group (for example -O, -F, -OH or -H). Take Ti$_3$C$_2$T$_x$ as an example$[8]$, when Ti$_3$AlC$_2$ is immersed in HF, the following simplified reaction will occur:

$$Ti_3AlC_2 + 3HF = AlF_3 + 3/2H_2 + Ti_3C_2$$  

(1)

$$Ti_3C_2 + 2H_2O = Ti_3C_2(OH)_2 + H_2$$  

(2)

$$Ti_3C_2 + 2HF = Ti_3C_2F_2 + H_2$$  

(3)

Using different concentrations of HF will result in the production of MXenes with different morphologies. The MXene etched with a high concentration of HF solution (15 mol/L) showed the morphology just similar with accordion, with the tiers being linked by van der Waals forces and hydrogen bonds. By using a low concentration of HF (15 mol/L), the morphology of MXene becomes a thick multilayer sheet with a smaller stacking gap. Experiments show that MXene diluted by HF etching always has a larger interlayer spacing and can maintain a higher mobility between layers, which makes it easier for ions to be absorbed by active sites, thereby exhibiting higher capacitance$[9]$. 

Figure 2. Schematic of the exfoliation process for Ti$_3$AlC$_2$. From ref. [9]

2.1.2. Fluoride salt and its derivatives etching

As an alternative to HF, the method of synthesizing MXene using a mixture of acid and fluoride salt is gentler, e.g. HCl/LiF, HCl/NaF, HCl/KF, HCl/NH$_4$F and(NH$_4$)HF$_2$[10]–[13]. Among which, the most commonly used and most effective etchant is HCl / LiF. MXene can insert ions, organic and inorganic substances between layers to increase the spacing between layers and weaken their bonding force to achieve the purpose of further separating thin layers. Studies have shown that lithium ions are inserted into MXene together with water molecules, and the interlayer spacing is increased (c~28Å), which can save additional layering steps.[14].
2.1.3. Electrochemical etching

Electrochemical etching is also one of the effective strategies for preparing MXene. It has been reported that Ti$_2$CT$_x$ can be synthesized by electrochemical synthesis from Ti$_2$AlC in a low-concentration hydrochloric acid solution. The termination ends of Ti$_2$CT$_x$ obtained by this method are -Cl, -O and -OH, but there is no -F, which will affect the performance of MXene.

2.1.4. from bottom to top

In 2015, Chuan Xu et al.[15] proved that the chemical vapor deposition (CVD) process can produce ultra-thin molybdenum carbide crystals with an in-plane size of up to 100 mm. And this defect-free Mo$_2$C also has two-dimensional superconductivity at low temperatures. Figures 4(c) and (d) exhibit the tungsten carbide crystals optical images and high-resolution transmission electron microscopy (HR-TEM), proving that this synthesis method is universal and can also be used to produce carbides other than Mo$_2$C. Therefore, this method can produce single-layer carbides and other MXenes.
Figure 4 (a) a schematic diagram of the growth mechanism. Molybdenum is dissolved in molten copper, and perfect $\alpha$-Mo2C crystals can be grown (as shown in the upper right picture). (b) Single layer of Mo2C (top) and 3nm thick $\alpha$-Mo2C crystal (bottom). (c) Optical micrograph of tungsten carbide crystals grown on copper/tungsten foil double layers by chemical vapor deposition. Scale bar, 10$\mu$m. (d) High-resolution transmission electron micrograph showing the ordered crystal structure of tungsten carbide crystals. Scale bar, 2 nm [15].

Obtaining MXenes by chemical etching is the most widely used method, while the bottom-up method has not been widely used due to the time-consuming research and slow progress.

3. Property and Applications

3.1. Electric properties

3.1.1. Electronic Conductivity

MXenes has ultra-high electronic conductivity, which can be used in electrochemical capacitor devices.[16]. MXenes was reported to have excellent electrical conductivity (no less than 14 000 S/cm reported for about 1 $\mu$m micrometers thin sheets) which can reduce power loss. The type of M element can affect the electronic properties. For example, when Ti$_2$C$_2$O$_2$ is replaced by Mo$_2$TiC$_2$O$_2$, the conductivity of the metal will be affected by the Mo element and it will be converted to a semiconductor according to its characteristics[17]. In addition, the defects in MXene will affect its conductivity as well. Carbon vacancies make Ti$_2$CT$_2$ have better electronic conductivity[18].
3.1.2. Terminations

By varying different terminals, the nature of MXenes can be modulated to produce more potential applications. The terminal species are related to conductivity. Controlling the surface terminations of MXene will be important for fabricating semiconductor or topological insulation MXene. However, so far, the semiconducting state and topological insulation state of MXenes have not been experimentally realized. The reason is that in general, the MXenes obtained by the current synthesis methods have mixed termination ends (-OH, -F, etc.); however, most superconductivity and topological states predicted by calculation require only one termination on the cover of MXene[19].

The mechanical characteristic of MXene largely depend on its surface termination. It has been reported that O-terminated MXene has high stiffness. But the elastic stiffness of O-terminated MXene is higher than that of MXene terminated by other groups (-F or -OH) [20]. This may be due to the fact that MXenes at different ends exhibit different lattice constants: generally, MXenes with F or OH ends have larger lattice parameters than those with O ends[21]. Moreover, the -OH terminal is unstable because the hydrogen atom at the -OH terminal tends to be take the place by alkali metal or transition metal species[22].

3.2. Mechanical and Physical properties

Some articles predict that MXenes will be stiffer and stronger than M3X2, but at present, since no real single-layer MXenes have been obtained for testing, thin films are generally used for that purpose. There is a report showed that the Ti3C2Tx films had hard mechanical strength. A ∼3.3-μm-thick Ti3C2Tx sheet was tested to have the tensile strengths of 22 ± 2 MPa, the Young’s modulus was 3.5 ± 0.01 GPa. Further introduction of PVA, the further the increase in strength. A hollow cylinder made of 90% (weight) Ti3C2Tx / PVA, made by rolling a Ti3C2Tx-based film with a diameter of 6 mm and a height of 10 mm, which can easily bear about 15,000 times as heavy as its original weight [23].

![Figure 5. Mechanical properties of flexible self-supporting Ti3C2Tx, Ti3C2Tx/PVA and cast PVA films.](image)

(a) The stress-strain curve of Ti3C2Tx/PVA film with different Ti3C2Tx content. (b) A cylinder with a diameter of 6 mm and a height of 1 cm, weighing 6.18 mg. (c) A hollow cylinder with a diameter of 6 mm and a height of 10 mm, weighs 4.75 mg, and is made of 90% (weight) Ti3C2Tx/PVA with a length of 35 mm, a width of 10 mm, and a thickness of 3.9 microns. The load used is nickel (5g), dime (2.27g) and 2.0g weight [23].
4. Applications

4.1. Batteries

Because MXenes has excellent electrical conductivity and vast specific surface area, it is very suitable for energy storage device applications. Among these MXenes, because the etching conditions of Ti$_3$C$_2$Tx are well known, and their physical and electrochemical properties have been studied theoretically and experimentally, Ti$_3$C$_2$Tx has become the main research focus of many researchers. For example, it is expected that Li$^+$ ions will diffuse rapidly on the surface of MXene, conducing to outstanding storage capacity and excellent high charge rate capability. The calculated capacities for Li on Ti$_3$C$_2$ are 447.8 mAh/g. Therefore, MXene has become a desired anode material for lithium-ion batteries[24], [25]. Moreover, a Ti$_3$C$_2$T$_x$ “paper” was synthesized by the intercalation with hydrazine monohydrate (HM) dissolved in N, N dimethylformamide (DMF), then filter. The “paper” acted a capacity of 410 mAhg$^{-1}$ at a 1C cycling rate and the capacity increased to 110 mAhg$^{-1}$ at 36C, respectively[26]. However, the surface terminal fluorination or hydroxylation, hinders the rapid delivery of lithium ions, thus greatly reducing the lithium capacity. Recently, Bingzhen Yan et al. showed through first-principles calculations that V$_2$CT$_2$ terminated by oxygen or sulfur, has excellent electrochemical properties, and maintains the metal conductivity. In addition, the large absorption energy and low diffusion barrier of Li atoms are found in V$_2$CT$_2$ (double bond O, S), which may give MXenes excellent energy storage capacity and charge-discharge rate. Therefore, V$_2$C decorated with oxygen/sulfur will become a promising anode material for lithium-ion batteries[27].

For the composed MXenes, Fan Zhang et al. reported a silicon/Ti$_3$C$_2$Tx MXene composite ruled by electrostatic self-assembly. The as-prepared composite can provide an original invertible capacity of 1067.6 mAh g$^{-1}$ when current is 300 mA g$^{-1}$. Furthermore, after 100 cycles, a stable cycle capacity of 643.8 mAh g$^{-1}$ was shown at 300 mA g$^{-1}$. The research provide inspiration for the synthesis of advanced energy density silicon anode materials applied in lithium-ion batteries[28].

Besides, there are other MXenes for metal (Na, K, Ca, Mg, and Al) batteries. Among these, compared with lithium, sodium ion batteries are abundant and low in cost. However, since the size of these ions are large, the diffusion in electrode materials is slow, the interposition/ejection behaviour in the active substance severely damages the intrinsic structure of the material, leading to short cycle life and defective rated performance, which hinders the expectation of large-scale use for energy storage[29].

4.2. Capacitor

MXenes can be inserted into its interlayer through polar organic molecules and metal ions. For example, various monovalent and multivalent cations (such as Li$^+$, Na$^+$, K$^+$ and NH$_4^+$) could be embedded in MXene (chemically or electrochemically) to participate in energy storage[30], [31].

Figure 6. the schematic of the capacitive and pseudocapacitive conditions [32].
Different electrolytes will have different effects on the principle of MXenes storing electric energy. There are two kinds of electrolytes: aqueous and nonaqueous. When the ions are in the aqueous electrolytes, and completely hydrated, an electric double layer can be formed without transferring charges between the electrode and the ions. Nevertheless, in the nonaqueous electrolytes, the ions are partially dehydrated and diametrically adsorbed on the MXene, and orbital hybridization with the surface-terminated specific will occur. It will cause the consumption of the electrostatic potential difference, mostly due to the redistribution of charges. This forms a pseudo capacitance. Figure 6 is the schematic of the capacitive and pseudocapacitive conditions. The stability and electronic state of surface adsorption are closely connected with the electrolyte and surface termination[32].

Figure 7 is the CV curve of MXenes in different electrolytes. In an aqueous electrolyte, the MXene electrode exhibits a rectangular CV curve (Figure 7c), which is a typical feature of EDL capacitor electrodes[33]. The in-situ X-ray diffraction (XRD) pattern of Ti$_2$CT$_x$ during charge and discharge shows the reversible change of the interlayer distanced (12.7 and 13.2Å, respectively), indicating that ions are embedded in the interlayer space. From ref. [32]

In contrast, the MXene electrode in the non-aqueous electrolyte exhibits fluctuating capacitance CV curves (Figure 7a,b)[34], [35]. This is similar to the CV curve expression of the redox peak. This may be due to the reversible Li$^+$ (de)intercalation. Therefore, the MXene electrode in the non-aqueous electrolyte exhibits intercalation pseudo-capacitance (redox capacitance). The convert in the apart between layers is very tiny, only about 0.1 Å, so the activated Ti$_2$CT$_x$ allows reversible Li$^+$ and Na$^+$ insertion/de-embedding into the interlayer space, and reversible Li$^+$ and Na$^+$ adsorption/desorption to each layer. On the surface of the sheet, ions are only inserted into the interlamination space.
5. Conclusion

MXenes as a advanced two-dimensional material, due to its outstanding characteristic (such as excellent surface area, adjustable electronic properties and extraordinary mechanical strength) has recently led to various aspects of its research, including synthesis, intercalation, electrical properties, Mechanical properties. Current research shows that M element will affect its electrical properties. For example, Mo element has more semiconductor properties than Ti. In terms of synthesis, the most widely used method is to use hydrofluoric acid and fluoride salt to selectively etch the A element layer to prepare multilayer MXenes. But one of the biggest problems is that high-quality single-layer MXenes cannot be prepared by this method. In addition, MXenes prepared by current synthetic methods have a variety of surface terminals, which limits its applications.

In comparison, because the internal layer of MXenes can accommodate various metal cations or NH4+ to store electrical energy and has the properties of low resistance and large interface area, it has become the best choice for future battery cathodes and supercapacitors. Among these MXenes, because the etching conditions of Ti3C2Tx are well known, and their physical and electrochemical properties have been studied theoretically and experimentally, Ti3C2Tx has become the main research focus of many researchers. However, how to balance various properties like energy density, power density, specific capacity, and lifetime to better store electrical energy is an area that should be studied in the future. In order to meet these challenges, the innovative work and practical applications of electrochemical energy storage still need to be further explored.

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