EMERGING MXENES MATERIALS FOR EFFICIENT SUPERCAPACITOR APPLICATIONS: CURRENT TRENDS AND FUTURE PERSPECTIVES

Abstract

In recent years, MXene has become one of the most advanced potential electrode materials used in high-performance supercapacitor applications. MXene nanomaterials possessed as an admirable capacity, required active surface area, flexibility, and outstanding mechanical qualities. MXene and related nanocomposites demonstrated their potential as new electrode materials. A wide variety of instances of MXene electrode materials are given in detail to further demonstrate the modifications brought about by these composites. This book discusses the most trends in the research of MXene-based SCs and their composites for supercapacitor applications. This chapter primarily addressed the electrochemical properties of composite electrode materials made of MXene and MXene-based compounds for energy storage applications.

Keywords: Two-Dimensional Material, MXene, Supercapacitor.

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I. INTRODUCTION

The rapid high-speed development of electronic devices in the modern societies the electrical energy is most important in the recent days. In these concerns, the sustainability, environmental freely and high efficiency energy conversion devices are required in this next generation lifestyles. Taking in this action, the electrochemical energy storage devices were helped to overcome these issues due to its specified with energy and power densities [1-5].

The EESDs were consists of capacitor, electrochemical supercapacitor, battery and fuel-cell. Based on the variation of energy and power density values the above-mentioned devices were categorised. Capacitor is one of the high-power density energy storage devices, which the charges were accumulates via dielectric medium. Batteries are considered as the off-middle energy and power density tools. In same way, fuel-cell as a high-energy density energy storage and conversion tool. Supercapacitor has a midway of energy and power densities in the EESD systems due to its special features of remarkable theoretical capacitance, long-life duration performance [6-10].

The achievement of high-performance in supercapacitors, we need to focus on the electrode material. In this connection, various (1D, 2D and 3D) dimensional based materials are involved in charge storage process. Herein, two-dimensional (2D) energy capacitive materials have the most crucial in the supercapacitor applications. Due to its outstanding mechanical, electrical, electronic, and chemical capabilities, single-layer atom-thick materials have made significant advances in a variety of industries, including semiconductors, electrodes, photovoltaics, water purification, etc.

Among them, graphene is a well-known and first 2D material to be found in 2004. Since its discovery, graphene has been the only material used in electronics and has attracted significant scientific interest.

In first of this group, a non-oxide, layered Ti_3C_2 ceramic, was created in 2011 from its 3D bulk crystalline Ti_3AlC_2 phase by a chemical process at room temperature. This was quickly followed and synthesised the more than a dozen other MXenes structures, an endeavour ambitious by worldwide skyrocketing deposition rates.

In this chapter contains the synthesis of MXene and their composites for advanced supercapacitor applications and to evaluate the characteristics performance and unique properties.

II. MXENE AS AN 2D MATERIAL

MXenes are new kind of two-dimensional compounds that are essentially stacked carbides, carbonitrides, and nitrides were combined with transition metals [11]. These are identified as $M_{n+1}X_n$ (n = 1, 2, or 3), Here "M" denotes an transition metal (ex. Sc, Ti, Zr, V, Nb, Cr, or Mo) as well as "X" denotes either carbon or nitrogen. Due to its sheet-like structure, the "ene" in MXene is modelled after graphene. More than one "M" may be present in them, and these "Ms" as ordered phases or solid solutions. On the other hand, representation of functionalized MXenes ($M_{n+1}X_nT_x$), the additional denotation "T" refers to free active group surface terminations (like -H, -F, = O and -OH) that were left over from the aqueous etchants (HF, H_2O, HCl) used throughout the selective etching of component "A" from their parent MAX phase [12-13]. The MXenes are given a hydrophilic quality by these terminations, which also significantly affects their electrochemical and dielectric properties. Furthermore, MXene with a specified termination and produced via chemical processing, intercalation and delamination, thermal annealing, and exfoliation techniques.

The MAX phases with unique layered structures and the formula as M_nAX_{n+1} (n = 1-3), herein, 'A' can be Al, P, Si, Ga, S, As, Ge, In, Sn, etc. In the MAX phase, the MX layer and the "A" layer are alternately layered. In contrast to the extremely strong M-X connection, the A element is bonded relatively weakly and more reactive, so selective etching eliminates it while leaving the MX arrangement intact [14]. MXenes are generated from the parent MAX phase lattice structure and feature hexagonal symmetry at the structural level. There are three main ways to prepare MXenes. One has a single M element, like Ti_2C and Mo_2C, another is a solid compound of one or more M phases arranged via randomly, like $(Ti,V)_2C_2$ and $(Cr,V)_3C_2$, and the last type is double-ordered M elements, like Mo_2TiC_2 and $Mo_2Ti_2C_3$, wherever also a single M element layer or two layers of a single M element are arranged midway the layers of the second M element. Accordingly, each of these MXenes can be represented as M_2X, M_3X_2, and M_4X_3, which are derivations of their respective MAX phases, M_2AX, M_3AX_2, and M_4AX_3, respectively. The construction of the MAX phases and their associated MXenes is seen in Figure 1.

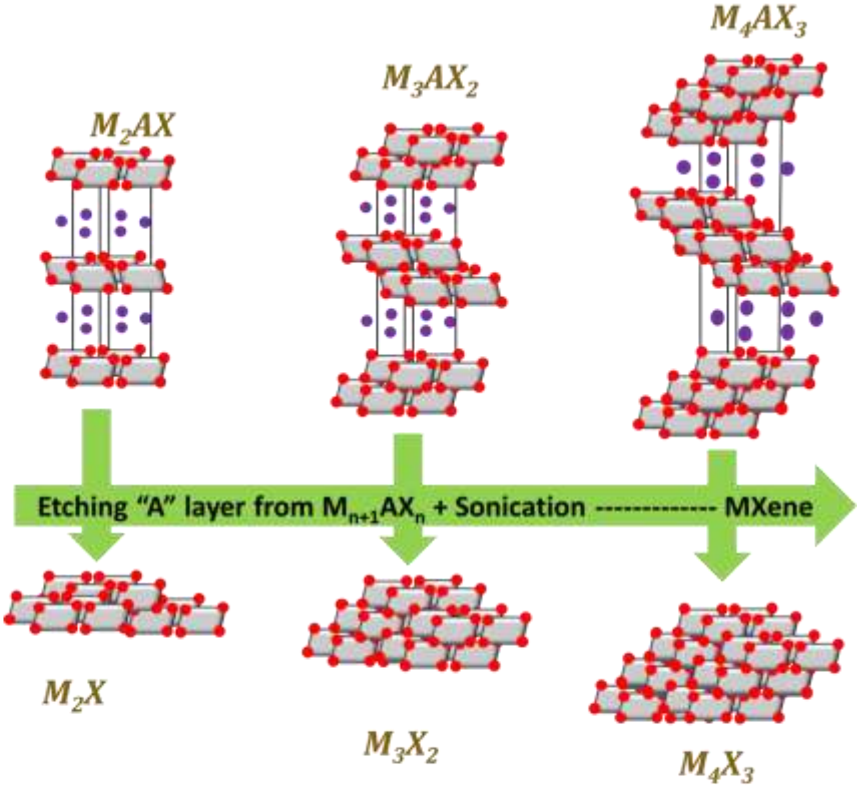

Figure 1: Structural Mxenes as a Different MAX Phase [15]

Figure 2 depicts the aforementioned procedure to remove the "A" element form the MXene nanostrutute. Other MXenes, as well as Ti_2C, Ta_4C_3, $(Ti_{0.5}, Nb_{0.5})_2C$, Ti_3CN, $(V_{0.5},$

$Cr_{0.5})_3C_2$, Ti_2C_3, and Cr_2TiC_2, were also synthesised using this technique. Alternative etchants for the preparation of various MXenes include NH_4HF_2 and a combination of LiF and HCl. As time went on, several efforts were made to generate various MXenes by utilising various etchants and etching processes. It goes without saying that key factors in chemical reactions include temperature, etching duration, etchant concentration, MAX phase particle size, and etching parameters.

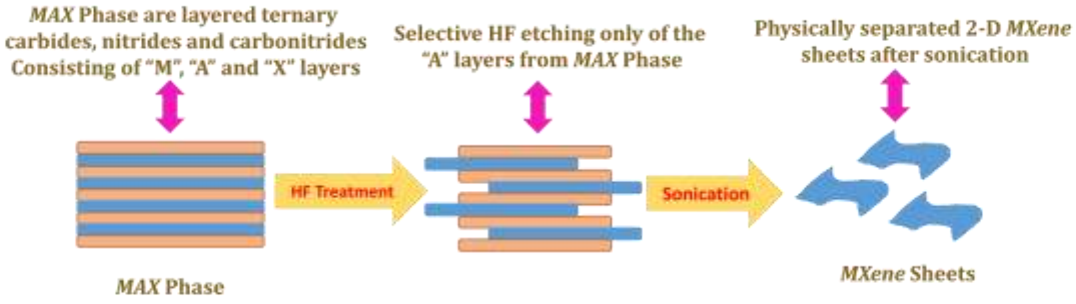

Figure 2: Scheme for MXenes from the MAX Phases Preparation Process [15]

III. MXENE – PROPERTIES

Due to their exciting combination of features, Mxenes - relatively the topical addition to the group of 2D materials - have raised a number of captivating problems for researchers from the various fields. Due to the fact that they are ceramic, they are stable mechanically and chemically in nature. They have large interlayer spacing, and larger than that of graphite, and their structural shapes include both mono-layer and multilayer structures. The thickness of the layers possible to modify in this structure. This open area midway the layers is accomplished of ion intercalation, that implies that ions of various sizes can be injected into this gap. This property is crucial for the material to be employed as a cathode in energy conversion applications [16-17].

Consequently, as the layered structure is moderately delaminated, it not only permits ion intercalation but also the creation of an electric double layer (EDL), which aids in charge storage in capacitors. The contact between MXene layers is primarily caused by hydrogen bonding and van der Waals attraction. Functional groups acting as terminations offer numerous chances to design the desired surface properties and aid in the regulation of their electrochemical, thermoelectric, and dielectric properties. Surface terminations transform the normally metallic MXenes into semiconductors like Sc_2CF_2, Sc_2CO_2, and Ti_2CO_2. Additionally, MXenes have extremely active transition components (M). The same can also be made using a variety of transition metals, each of which can be customised for a variety of purposes [18]. Direct functional theory has estimated that some of these MXenes have in-plane elastic constants above 500 GPa, that is higher than the stiffness of routinely used structural steel, which is 400 GPa [19]. The MXenes must have excellent physical characteristics, mechanical, electrochemical, ion mobility, and electronic transport properties in order to be used as electrode materials.

The 'M' atoms serve as the source of their electrical characteristics. Surface functionalized MXenes often exhibit semiconducting nature, while all unfunctionalized

MXenes exhibit metallic nature. Sc-based MXenes such Sc_2CF_2, $Sc_2C(OH)_2$, and Sc_2CH_2 nanotubes and Mo_2CT_x films have been proven to have semiconductor-like characteristics using Density Functional Theory (DFT) optimised computations. It was discovered that the Ti vacancy defects were responsible for the high conductivity of Ti-based MXenes such $Ti_3C_2T_x$. In addition to their use in energy storage devices, their high conductivity property has opened them up for possible applications as transparent conductors, magnetic materials, superconductors, absorbents for heavy metals, and flexible electronic devices.

MXenes have previously been experimentally included for a variety of prospective uses, including rechargeable batteries, ultracapacitors, field effect transistors, hydrogen storage, sensors, catalysts, electromagnetic interference shielding and biomedical devices [20].

IV. MXENE – SYNTHESIS PROCESS

There are two methods for synthesising MXenes. In top-down process, thin layers of MXene films are exfoliated from their MAX phase/non-MAX phase components, whereas in the bottom-up method, diverse materials are mixed to generate MXene thin films.

The synthesis procedures determine the structure, features, and qualities of MXene. Figure 3 is a flow diagram categorising several top-down and bottom-up synthesis methods of MXenes.

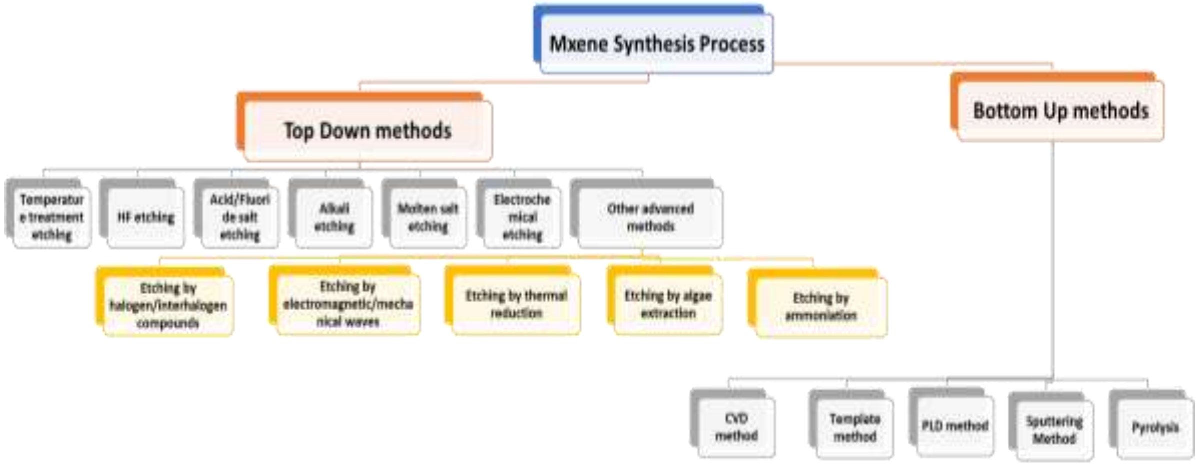

Figure 3: Top-Down and Bottom-up Synthesis Approaches of Mxene [21]

V. MXENE FOR ENERGY STORAGE APPLICATION

The demand for energy storage technologies like batteries and supercapacitors was expected to increase gradually over the present years to the industrial trends. At the same time the living society was moves away from the burning fuels for energy generation towards that renewable sources like wind and sun, among others. They have a wide range of uses, from small electric mobility systems and handheld electronics to big electric grid systems [22].

The most widely used electrochemical energy storage (EES) solution is batteries, but they also have a lot of problems. These batteries raise a number of unique safety and cost issues. They suffer from extremely long charge times as well. Because of their wider availability and multivalent nature of the battery electrodes were reached an effective limits and better devices utilising for different metal ions, such as Na, K, Mg and Ca, etc. Improved development and selection of electrode and electrolyte materials are also necessary for these more recent systems in order to achieve maximum efficiency [23].

There are various obstacles to the development of LIBs and supercapacitors, but two are particularly significant: 1. Obtaining high energy and power density simultaneously for these devices is rather challenging. 2. There is a clear shortage of resources, which is causing supply chain problems, which are raising their prices [24]. Furthermore, the problem of utilising and storing the obtained energies becomes a bigger size and has pushed in the researchers through including the effective devices for achieving the maximum efficiency.

Supercapacitors and rechargeable batteries both have advantages and disadvantages when it comes to functionality in the various electronic tools. In exchange for low power densities, batteries produce extremely high energy densities. In contrast, supercapacitors have relatively low energy densities and superior power densities in addition to a quick charge-discharge rate. In order to researchers have worked a lot to develop the electrodes that can deliver a combination of longer life cycles, high energy densities, and high-power densities [25]. These qualities have been made possible by Mxenes due to its good capable energy storage phenomena. Here are a few study findings that confirm MXenes and various structures were worth able materials for innovative supercapacitor devices.

VI. MXENE FOR SUPERCAPACITOR APPLICATION

Supercapacitors are likely capacitors with a capacitance that is between that of capacitor and batteries. In comparison to a standard rechargeable battery, they provide charges faster and have longer charge-discharge cycles. Supercapacitors can be broadly classified into two types, each with a unique method for storing and transferring charge storage process [26].

Some supercapacitors operate without going through phase shift; instead, they use redox processes, intercalations, and electro absorption, which are quite quick and offers the batter electrochemical performance. Supercapacitors were literally classified in two types, i.e, pseudocapacitors and electrical double layer capacitors (EDLCs), that is an essentially function by generating the layer in the midway of the electrode surface and electrolyte. This interface's capacitance increases with the specific surface area in this model. Carbons and various carbon sources, such as activated carbon and graphene, are the most common materials used as electrodes in EDLCs.

Traditional materials for pseudocapacitors, such as MnO_2, MoO_3, Nb_2O_5, RuO_2, etc., have an admirable capacitance, even so, they possessed the poor electrical conductivity. MXenes were made significant advancements in an electrochemical supercapacitor. Due to their distinct structure and electrical characteristics make them ideally well-matched for supercapacitor applications. Table 1 represents the pure MXene and their electrochemical properties in supercapacitor applications.

S. No	Electrode	Etchant	Electrolyte	V_c (F cm^{-3}) vs (mV s^{-1})	Retention (%)	Cycling Retention (in Cycles)	Ref.
1	$Ti_3C_2T_x$	HF	1 M KOH	340 vs 20	62.2	100 % (10,000)	27
2	$Ti_3C_2T_x$	HCl/LiF	1 M H_2SO_4	910 vs 2	81.3	100 % (10,000)	28
3	d-$Ti_3C_2T_x$	HF	1 M H_2SO_4	520 vs 2	42.3	100 % (10,000)	29
4	KOH-400-$Ti_3C_2T_x$	HF	1 M H_2SO_4	517 vs 1	-	99 % (10,000)	30
5	MXLLC	HCl/LiF	3 M H_2SO_4	200 vs 2	-	100 % (20,000)	31
6	$Ti_3C_2T_x$	NaOH	1 M H_2SO_4	511 vs 2	-	89 % (10,000)	32
7	$Ti_3C_2T_x$ hydrogel	HCl/LiF	3 M H_2SO_4	1500 vs 2	56.8	90 % (10,000)	33
8	$Ti_3C_2T_x$ hydrogel	HCl/LiF	3 M H_2SO_4	226 vs 1	83.1	95 % (10,000)	34
9	$Ti_3C_2T_x$ aerogel	HCl/LiF	1 M KOH	87.1 vs 2	76.6	97 % (10,000)	35
10	MXene – C12	HF/LiCl	EMIMTFSI	492 vs 1	38.9	95 % (10,000)	36

VII. CONCLUSION

MXene, a brand-new two-dimensional substance, has generated considerable interest in numerous fields due to its excellent mechanical, electrical, and especially electrochemical capabilities, much like graphene. This special features of the Mxene will be widely used in the next generation of extremely effective electrochemical devices in an EES systems, that is greatly needed in small-scale portable electronic devices, mobile phones, and tablets. Moreover, MXene and their composites were approaches as an advanced materials in the range of aqueous electrolytic parameters, including admirable capacitance, long-time cycle operation, good structural retention, effective power and energy densities, vast mechanical and thermal stability performance. To ensure that technology is broadly implemented at minimal environmental free, low cost and structural stability in future.

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