TOPICAL REVIEW

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To cite this article: Ayomide Adeola Sijuade et al 2023 Nanotechnology 34 252001

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IOP Publishing Nanotechnology

Nanotechnology 34 (2023) 252001 (16pp)

https://doi.org/10.1088/1361-6528/acc539

Topical Review

Vanadium MXenes materials for nextgeneration energy storage devices

Ayomide Adeola Sijuade¹, Vincent Obiozo Eze¹, Natalie Y Arnett¹ and Okenwa I Okoli^{1,2,*}

E-mail: okoli@eng.famu.fsu.edu

Received 30 September 2022, revised 12 December 2022 Accepted for publication 17 March 2023 Published 11 April 2023



Abstract

Batteries and supercapacitors have emerged as promising candidates for next-generation energy storage technologies. The rapid development of new two-dimensional (2D) electrode materials indicates a new era in energy storage devices. MXenes are a new type of layered 2D transition metal carbides, nitrides, or carbonitrides that have drawn much attention because of their excellent electrical conductivity, electrochemical and hydrophilic properties, large surface area, and attractive topological structure. This review focuses on various synthesis methods to prepare vanadium carbide MXenes with and without etchants like hydrofluoric acid, lithium fluoride, and hydrochloric acid to remove the 'A' layers of the MAX phase. The goal is to demonstrate the utilization of a less toxic etching method to achieve MXenes of comparable properties to those prepared by traditional methods. The influence of intercalation on the effect of high interlayer spacing between the MXene layers and the performance of MXenes as supercapacitor and battery electrodes is also addressed in this review. Lastly, the gaps in the current knowledge for vanadium carbide MXenes in synthesis, scalability, and utilization in more energy storage devices were discussed.

Keywords: 2D materials, transition-metal carbide, MXene, synthesis, batteries, supercapacitors

(Some figures may appear in colour only in the online journal)

1. Introduction

Humanity's survival depends on efficiently producing, storing, and utilizing the available fuels needed for energy production in an environmentally benign manner [1, 2]. The increasing use and demand for energy in association with the issues related to global warming and the depletion of fossil fuels have encouraged the switch to alternative and reliable sources of energy and energy storage devices [3]. This issue has resulted in seeking effective methods for developing advanced catalysts and electrode materials [4] utilized in energy storage devices like batteries [5], capacitors [6], and supercapacitors [7]. Nonetheless, the upscale of the following energy generation and storage materials depends

on the production costs, stability, efficiency, and safety of the various electrode materials used in their manufacture. The most efficient electrode materials tested are noble metals like ruthenium, iridium, platinum, and their composites; however, severe limitations in the practical day-to-day application of the metals still exists due to their high cost and scarcity [8–12].

Over the years, alternative research on micro and nanomaterials as electrode materials has attracted much attention. These materials are characterized to allow for easy electron transport, high surface area, increased rate of reaction, and better intercalation strain accommodation [13]. The utilization of lithium-ion [14] and alkaline [15] batteries have led to a tremendous breakthrough in energy storage devices. However, the inherent limits of these micro and nanomaterials have failed to meet the ever-rising electricity needs.

¹ High-Performance Materials Institute, FAMU-FSU College of Engineering, Tallahassee, FL 32310, United States of America

² Herff College of Engineering, University of Memphis, Memphis, TN, 38111, United States of America

^{*} Author to whom any correspondence should be addressed.

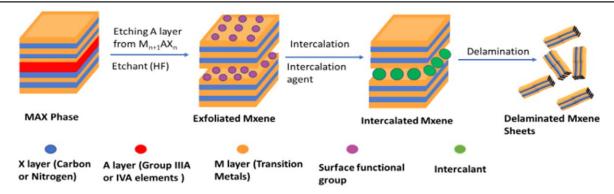


Figure 1. Schematic diagram of MXene synthesis from MAX phase.

Micromaterials' intrinsic properties and single-phase nanomaterial's weak mechanical stability, low conductivity, and unwanted side reactions have disadvantaged these batteries from fulfilling the energy requirements [16–18]. The continuous search for highly active, low-cost, and stable materials with exceptional charge transfer efficiency has led to numerous carbon-based derivatives [19], conducting polymers, and metal oxides discovery. These include carbon nanotubes [20], graphene [21], magnesium oxide [22], activated carbon [23], and ruthenium oxide [24].

Although carbon presents as a widely used cheap, non-toxic material with a large specific area and an easy synthesis route, when activated, its capacitance is hindered by the various pore sizes gotten during the process. This limits its energy density, conductivity, and capacitance by impeding ion passage across a particle in supercapacitors [18, 25–27]. A good example is graphene, with a high theoretical specific surface area of 2630 m² g⁻¹ while only reaching an actual capacitance of 330 F g⁻¹. This can be attributed to the irreversible self-stacking and the clustering of graphene sheets during the electrochemical and electrode fabrication process [28].

Ruthenium oxide has good electrical conductivity, mechanical strength, frequency response, and stability but has a high fabrication cost [26, 29]. To improve the cost-effectiveness, Han *et al* fabricated RuO₂.coated vertical graphene hybrid electrodes for supercapacitors with an aerial capacitance of 2143 F g⁻¹ [29]. However, ruthenium remains an expensive precursor for electrode materials. The high cost of ruthenium oxide has opened doors for alternatives such as magnesium oxide (MgO) as electrode materials. Feng *et al* reported MgO's excellent cycling capability with a capacity retention rate of almost 100% after 10000 cycles. On the other hand, graphene is a good conductor of electricity and heat and is extremely lightweight and robust [21]. However, the graphene layers get clustered easily, inhibiting the free flow of electrolyte ions [30].

Research into improving the physical and chemical properties of 2D materials led to the discovery of the first MXenes Ti₃C₂T_x in 2011 by Gogotsi and coworkers [31]. MXenes have been called wonder materials due to their unique microstructures and abundant surface terminations resulting in fantastic electrical, mechanical, and thermal properties [32]. V₂C MXenes are stable at 150°C in air and temperatures up to 375°C in an argon atmosphere. However, the V₂C MXene oxidizes with a temperature increase to form

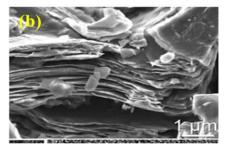
nanoparticles containing vanadium trioxide V₂O₃ and vanadium carbide V₈C₇ [33]. MXene flakes have the formula $M_{n+1}X_nT_x$ (n=1, 2, or 3), where M stands for early transition metals interwoven with carbon or nitrogen layers (X). Figure 1 shows a schematic illustration of a typical MXene synthesis process with an acid exfoliant. As shown in figure 1, the selective etching of A layers (group IIIA or IVA elements like Al and Si) from the MAX phase results in the synthesis of MXenes. The MAX phase comes from a family of ternary carbides and nitrides with the formula $M_{n+1}AX_n$ (n = 1, 2, 3), with M and X being the same as MXenes but A layers representing an element from group IIIA or IVA [34–36]. Depending on the synthesis method, the T_x represents the different functional groups like hydroxyl, oxygen, or fluorine [37–40]. Density functional theory calculations predicted that MXenes with OH, O, or F terminations are semiconductors with a bandgap range of 0.05-1.8 eV. Whereas bare MXenes are predicted to be metallic conductors [41]. Due to the diversity of transition metals that MXenes possess, around 30 types are reported, and about 70 are theoretically projected. MXenes applications include wearable sensors, nuclear waste treatment, gas sensors, hydrogen storage, photocatalysis, batteries, and hydrogels [42–47]. Much research has gone into using MXenes for energy storage devices due to their excellent conductivity, large surface areas, environmentfriendly nature, and good rate capabilities [48].

Vanadium carbide MXenes (V_2C) are fascinating due to their lightweight, pseudocapacitive behavior, high Li-ion intercalation capacity, and conductivity [49, 50]. Vanadium MXenes also have a greater interlayer spacing than as-prepared Ti- and Mo-based MXenes, which is advantageous for energy storage intercalation and deintercalation [51]. In addition, the various valence states of +2, +3, and +4 of the vanadium MXenes have proven advantageous for electrochemical performance as supercapacitor electrodes [52]. This paper focuses on the review of V_2C MXenes, the synthesis, structure, properties, applications in energy storage devices, and the issues with commercializing their use.

2. Synthesis of vanadium carbide MXenes

MXene synthesis involves the selective etching of the A layers of the MAX phase precursors (figure 1). There are two bonds in





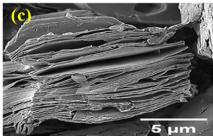


Figure 2. SEM images of V₂CT_x MXene etched with HF by (a) Reprinted (adapted) with permission from [43]. Copyright (2019) American Chemical Society. (b) Reprinted (adapted) with permission from [41]. Copyright (2013) American Chemical Society. (c) VahidMohammadi *et al* Reprinted (adapted) with permission from [59]. Copyright (2017) American Chemical Society.

MAX phase structures: the M–X and M–A bond. Due to the strong bond between the M-X layers, separating them through mechanical shearing is difficult. However, the M-A bonds can be separated through selective etching of A layers due to their chemical activity, which is critical in making MXenes [53]. It is also important to note that etching is a kinetically controlled process; therefore, each MXene needs different reaction times and temperatures to complete conversion depending on the MAX phase [53–56]. Typically, MXenes with larger n in $M_{n+1}C_nT_x$ translate to a more significant number of transition metals and carbon atoms needing stronger etching or longer duration. An example is $Mo_2Ti_2AlC_3$ (n = 3) which requires an etching time double its counterpart Mo_2TiAlC_2 (n = 2) under the same etching conditions [53], and $V_4C_3T_x$, which requires an etching time of 96 h compared to the V₂CT_x etched for 8 h [46, 48]. In addition, the synthesis method adopted determines the position of the peaks, which depends on the amount of trapped water between the MXene layers. V₂C MXene synthesis has been explored through various methods, including etching with HF [43], NaF [33], LiF [57], and electrochemical etching [58].

2.1. Hydrogen-fluoride etching

The first successful etching of V₂CT_r was done by Naguib et al [41] using HF on V₂AlC, they achieved a yield of 90% after etching for 9 h. Since then, other researchers have successfully synthesized V₂CT_x with HF and have used it for hydrogen evolution, batteries and gas sensors [43, 59, 60]. The V₂C MXenes synthesized with this method are usually multilayered, accordion-like structures with XRD peaks corresponding to (0002) planes [41, 43, 59]. Figure 2 shows the SEM image similarities of V₂C MXenes synthesized with the HF method. Using atomic force microscopy (AFM), Lee et al found that the single-layer flakes had a thickness of \sim 1.75 nm after delamination [43], which correlates to \sim 1 nm reported by Naguib et al and a yield of 60% [41]. HF is highly selective and has good etching qualities, so much so that it can selectively etch cubic SiC. This process can be upscaled to manufacture nanodevices such as cellular probes and sensors [61, 62]. However, HF's acute toxicity prevents the large-scale synthesis of MXenes through this method and, ultimately, the comprehensive utilization of MXenes in energy-related applications [58]. Also, high levels of HF can significantly irritate the eyes, skin, and nasal passages. Lastly, high concentrations may infiltrate the lungs and result in excessive bleeding and edema. To prevent these issues, other methods of MXene synthesis are explored.

2.2. Hydrogen-fluoride free etching

2.2.1. Etching with fluoride salts. As an alternative to etching V₂CT_x with HF, strong acid and a fluoride salt can be used to form in situ HF that etches the A layers [53]. Guan et al demonstrated the good etching ability of LiF + HCl for 120 h to produce uniform multilayered, high-purity MXene sheets [57]. TEM images in figure 3 reveals that the distance between the parallel planes of the MXene sheets (d-spacing) is about 0.97 nm. It was also observed that the MXenes have large and thin flakes with no pores or particles found on the surface, consistent with the V₂C MXenes etched in KF + HCl, (NH₄)HF₂, and NaF + HCl solutions [57]. Wu et al found that NaF + HCl is the most efficient fluoride salt used in etching compared to LiF + HCl, NaF + HCl, and KF + HCl [33]. After etching with HCl and NaF, Liu et al discovered that etching with fluoride salts results in purer MXenes due to the intensity ratio of V_2 AlC's (002) peak to V_2 C's (002) peak (I_{MAX}/I_{MXene}) value of 4.11% [63]. This result indicates that more MXenes were converted from the MAX phase using NaF + HCl as there was a decrease in the ratio of the MAX phase to MXene after 72 h, making NaF + HCl better than any other method of etching. SEM images of the synthesized MXenes reveal a quasi-2D structure with thin layers, as shown in figure 3(c) [63]. It is important to note that different fluoride salts require unique etching times (120 h for LiF + HCl etching and 72 h for NaF + HCl etching) [46, 51]. The molten salt environment also provides a viable and green chemistry for the synthesis of MXenes [64]. The traditional MXene phases can also be synthesized with Molten ZnCl_{2.} The Cl- terminated MXenes are expected to be more stable than the F-terminated MXenes which should improve the energy storage applications. However, V₂CCl, could not be synthesized due to the higher M-A bonding strengths than Ti₃ZnC₂, and Ti₂ZnC [64]. The equation for the reaction is proposed below;

$$V_2AlC + 3ZnCl = V_2C + 3Zn + AlCl_3.$$
 (1)

2.2.2. Electrochemical etching. Electrochemical etching (Eetching) resolves the issues associated with HF toxicity. Herein, V_2CT_x was etched using 0.4 V to 0.7 V to create the

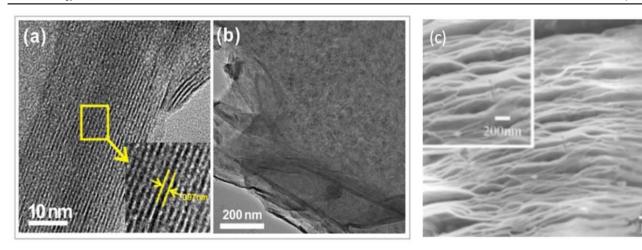


Figure 3. (a), (b) TEM images of V_2C etched with HCl and LiF. Reproduced from [57]. © IOP Publishing Ltd. All rights reserved. (c) SEM image of V_2C after 72 h. Reproduced from [63]. © IOP Publishing Ltd. All rights reserved.

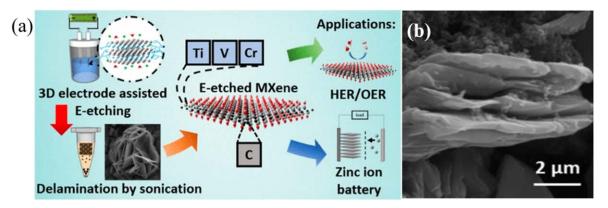


Figure 4. (a) Electro-etching method and the applications (b) V_2CT_x synthesized with electrochemical etching. Reprinted (adapted) with permission from [58]. Copyright (2019) American Chemical Society.

MXene under fixed conditions of (1 M/50 °C) for 9 h as seen in figure 4(a). The optimized voltage for etching was 0.5 V resulting in V_2CT_x MXenes with a micro-size of 25 μ m and a flower-like architecture. The synthesized MXene exhibited a specific capacity of 100 mhA g⁻¹ [58]. Figure 4(b) shows the layered MXene structure achieved after synthesis depicting the accordion-like structure with a lateral size of $>1 \mu m$ and thickness of 5-80 nm. It was also noticed that MXenes E-etched had substrate-driven architectures and can be very useful for forming various 3D composites [58]. However, lower yields (~50%) and residual MAX precursors were obtained from the E-etched method, uncharacteristic of other solvent-based methods. Since the by-products from this method can be recycled, the yield can be improved by recycling the sediments of the MAX phase, which can increase the conversion rate to $\sim 75\%$ [58].

2.2.3. NH_4HF_2 etching. Another method to reduce the toxicity of HF is replacing it with relatively mild NH_4HF_2 [65]. The etching reactions are shown in equations (2) and (3) below [2];

$$M_{n+1}AX_n + 3NH_4HF_2 = (NH_4)AlF_6 + 3/2H_2 + M_{n+1}X_n$$
 (2)

$$M_{n+1}X_n + aNH_4HF_2 + bH_2O$$

= $(NH_3)_C(NH_4)_dM_{n+1}X_n(OH)_XF_y.$ (3)

This method does not require a delamination step as NH⁴⁺ is inserted between the MXene nanosheet layers which increases the interlayer spacing [2]. Feng *et al* synthesized Ti₃C₂ MXenes using NH₄HF₂ to obtain larger interlayer spacing, improving the space for ion-embedded Ti₃C₂ to be stored. The MXenes were synthesized by adding 1g Ti₃AlC₂ to NH₄HF₂ and were stirred at 60°C. The etched products were then washed in deionized water until a neutral pH was reached. From the results, Ti₃C₂ etched with NH₄HF₂ had better pseudo capacitance with a specific capacitance of 78 F g⁻¹[66]. Even though NH₄HF₂ has been used to synthesize titanium-based MXenes, its utilization is lacking for vanadium-based MXenes to the best of the writer's knowledge. Further research is required to develop this synthesis process for vanadium-based MXenes.

2.3. Delamination

After synthesis, delamination of the MXene layers is significant because the resulting layers are held together by Van

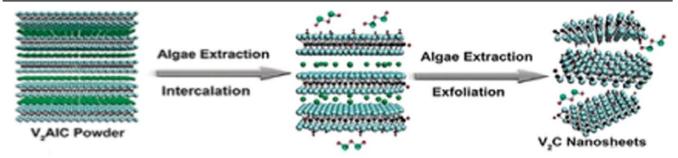


Figure 5. Schematic diagram of V₂C by algae extraction from Zada *et al* Reproduced from [68] with permission from WILEY-VCH, copyright 2020.

Vanadium carbide MXenes Titanium carbide MXenes Particle Etching time Particle Etching time Method of synthesis Yield size (hours) Yield size (hours) References HF etching 60% 8 80% 10 [41, 69] $< 1 \mu m$ $2 \mu m$ 120 $\sim 100\%$ LiF + HCl 91.3% 10 [57, 70] $<1 \mu m$ $\sim 1 \mu \text{m}$ NaF + HCl > 90% 84% 48 $<1 \mu m$ 72 $2 \mu m$ [63, 71]KF + HCl87% $11.8 \mu m$ 3 No No yield [33, 72] yield Electrochemical 50% $25 \mu m$ 9 >90% $18.6 \mu m$ [58, 73] etching I, Br +HCl N/A N/A 71% $1.8 \mu m$ [74]

Table 1. Yield, particle size, and applications of MXenes synthesized with different methods.

der Waals or hydrogen bonds, preventing the single flakes from forming. Delamination/exfoliation subjects the MXene layers to further treatment, allowing the formation of single flake MXene layers. First, the MXenes are intercalated with ionic or organic molecules and/or inorganic cations, followed by handshaking or ultrasonication for a while. Naguib et al investigated the intercalation of vanadium carbide (VC) MXenes with tetrabutylammonium hydroxide (TBAOH). It showed that a peak shift and an overall decrease in the dspacing occurred, which confirms the delamination of the MXenes [67]. Other compounds like choline hydroxide and n-butylamine also successfully delaminated the MXene sheets [67]. Zada et al explored green delamination using algae. Figure 5 shows the synthesis procedure of the delaminated MXene sheets using the algae extraction approach. The delamination resulted in MXene sheets with good structural stability, a high absorption rate, and a yield of 90% [68]. Based on the above-discussed MXene synthesis methods, table 1 below compares the yield, particle size, and etching time for different synthesis methods for titanium and vanadium MXenes.

2.4. Solid-solution MXenes

A class of double transition metal (DTM) MXenes was discovered in 2015 by combining two transition metals in an ordered structure. This entailed sandwiching one or two layers of a transition metal (M') between two layers of another transition metal (M') [75]. These phases exhibit out-of-plane ordering in M_3C_2 and M_4C_3 MXenes and have been

computationally predicted to be stable [75]. However, not many have been synthesized or characterized, some of which include Mo_2TiC_2 and $Mo_2Ti_2C_3$ [76, 77] with even fewer studies done on DTM with randomly mixed transition metal atom (solid solutions) [75]. Studies have predicted that DTM structures would result in a modification of the electronic state of the metal layers, improve electrical conductivity, and catalytic activity or pseudo-capacitive charge storage [78]. Single-phase V_2CT_x has been studied as electrodes in supercapacitors, lithium-ion, zinc-ion, and aluminum-ion batteries. However, the electrochemical properties of solid-solution MXenes are less known with M_2XT_x not reported [79].

Wang et al synthesized two series of niobium-containing solid-solution MXenes, $Ti_{2-\nu}Nb_{\nu}CT_{x}$ and $V_{2-\nu}Nb_{\nu}CT_{x}$ (y = 0.4, 0.8, 1.2, and 1.6), investigated their electrochemical properties and compared them to corresponding single-metal MXenes $(Ti_2CT_r, Nb_2CT_r, and V_2CT_r)$ [79]. It was discovered that modifying the M-site chemistry tuned the capacitive behavior and cycling stability of the MXenes. Also, as the niobium content increased, the redox peak prominence decreased while the cycling stability was enhanced [79]. Another study by Wang et al [80] studied the performance of V₃CrC₃T_x MXenes as anodes in Zn-ion supercapacitors. It was found that partially replacing Cr atoms for V atoms in $V_4C_3T_x$, caused an increase in the interlayer spacing of the MXenes, which in turn caused an increase in the adsorption of Zn ions and ion diffusion. This improved the capacitance, discharge potential and cycle stability of the

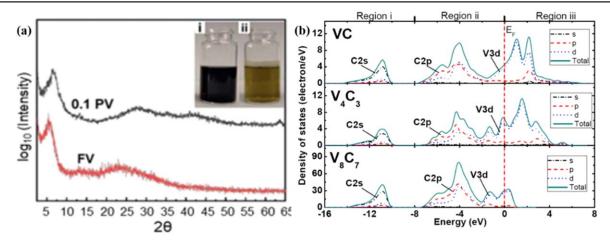


Figure 6. (a) XRD patterns of untreated- V_2CT_x (red) samples and 0.1 M polyphosphate- V_2CT_x (black). Pictures on the top right show (i) 0.1 M polyphosphate- V_2CT_x (left) sample and (ii) untreated V_2CT_x sample (right) after three weeks of exposure to ambient air. [84] John Wiley & Sons. [© 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim]. (b) total density of states (TDOS) and partial density of state (PDOS) for VC, V_4C_3 , and V_8C_7 . Reproduced from [85]. © IOP Publishing Ltd. All rights reserved.

synthesized batteries. They also demonstrated outstanding mechanical flexibility with an ultra-high area energy density of 51.12 μ W h cm⁻², long cycle life of 20 000 cycles (84.5% capacitance retention), and bendability of 10 000 cycles (80.2% capacitance retention) [80]. Different compositions of Mo_xV_{4-x}C₃ with x = 1, 1.5, 2, and 2.7 were synthesized by Pinto *et al* [75]. It was discovered that varying the Mo:V ratio, the electrical, electrochemical, and surface termination ratios (O:F ratio), can be tuned. The highest of these ratios was the Mo_{2.7}V_{1.3}C₃ composition which showed a volumetric capacitance of 860 F cm⁻³ and a high electrical conductivity of 830 S cm⁻¹ at room temperature [75].

3. Structure and properties of vanadium carbide MXene that make them suitable for energy storage devices

V₂C MXenes have a closely packed structure before delamination, similar to their MAX phase precursors. The X atoms partially fill the octahedral vacancies of the face cubic center (fcc) sublattice, which makes them have structural deficiencies [47, 81]. The crystalline structure resembles the NaCl cubic structure, as seen in figure 6, with a disordered δ -VC_{1-x} (VC_{0.65}-VC_{0.90}) extensive homology. The high structural deficiencies make V₂C MXenes suitable for electronic applications [81]. The structural defects may lead to atomic ordering connected to the rearrangement of nonmetallic atoms and structural vacancies at interstitial lattice positions. Shacklete et al showed that the resistivity of vanadium carbide in the disordered phase is increasingly higher than in the ordered phase due to the disordered phase transition [82]. Therefore, the ordered phase is more suitable for electrical and energy storage applications. This finding suggests that the ordering from the structural deficiencies found in vanadium carbide is highly significant. Theoretically, V-based and vanadium-containing MXenes have a higher electrochemical theoretical capacity than the popular $Ti_3C_2T_x$ MXenes in batteries. Realizing the high theoretical capacity depends on the high purity V_2C MXene; however, this is difficult to achieve. The difficulty of synthesis arises from the higher formation energy of V_2C from V_2AlC compared to other MXenes [63]. This high theoretical capacity might be due to vanadium's rich valence charges from +2 to +5. Due to the formation of structural vacancies in vanadium carbide and the unique ordering of the carbon atoms in its structure, V_2C MXenes are responsible for increasing microhardness and electrical conductivity [83].

Vanadium carbide has six solid single-phase zones: VC, α -V₂C, β -V₂C, V₄C₃, V₆C₅, and V₈C₇. Each of these has a different resistivity depending on the ordering. Because of their narrow band gaps, all vanadium carbides (VC) MXenes have metallic properties at the Fermi level. Although a covalent bond exists between the transition metal and carbon, V₂C MXenes also has metallic and ionic properties, resulting in a high melting point, good corrosion resistance, high hardness, and good electrical conductivity [82]. However, as demonstrated by other MXene types, V₂C MXenes are highly unstable due to the –OH, –O, or –F terminations formed due to the etching process.

Usually, oxidation starts at the edges and gets defective in the presence of oxygen and water [53]. This property strongly hinders practical use and warrants special storage conditions in dark, low-temperature, non-aqueous environments to prevent oxidation. In addition, edge binders may be used to increase the material's shelf life [86]. Iqbal et al revealed that using polyanionic salts, such as polyphosphates (P), polysilicates (Si), and polyborates (B) as edge binders drastically improved the shelf life of vanadium and titaniumbased MxXnes [87]. In particular, the shelf life of V₂CT_x drastically improved with the use of polyphosphate [87]. Figure 6(a) shows the XRD patterns of V₂CT_x treated with 0.1 M polyphosphate(black) and untreated V₂CT_x. The XRD graphs show that the V_2CT_x synthesized with 0.1 M polyphosphate salt and stored under vacuum had the (002) and (110) peaks near 6° and 64°, respectively, which are

characteristic peaks of V₂CT_x. Also, no other peaks were observed, indicating that at the XRD level, neither case detected oxidation. However, no V₂CT_x diffraction peaks were obtained from the V₂CT_x with no added salt. This issue might be because of the dissolution of V₂CT_x due to the presence of V₂O₅. It can also be seen from figure 6(a) that there is a characteristic color difference between the sample with polyphosphate salt (figure 6(a) (i)) and without the polyphosphate salt (6a (ii)). The V₂CT_x suspension without the salt oxidizes and gives off the characteristic orange color of dissolved V⁵⁺ ions in the water. At the same time, the polyphosphate salt sample did not experience any color change compared to a new colloidal suspension [87]. Another study by Natu *et al* demonstrated polyanionic salts as edge binders to mitigate oxidation [84].

It was discovered that among the salts tested, polyphosphates, polyborates, and polysilicates, polyphosphates salts were the best at suppressing MXene oxidation for up to three weeks in the air, as illustrated. Additional advantages associated with polyanionic salts include low-cost and easy purification [84].

3.1. Intercalation mechanism in MXenes

Intercalation was first reported in 1957 by McDonnell et al without explaining how it works [88]. Over the years, research on intercalation has resulted in it being defined as the reversible uptake of guest molecules in chained or layered structures due to weak intercalation. During intercalation, the lattice swells, and the chain structure is not as stable as the layered structure, which may cause disintegration. A significant characteristic of intercalation is that the insertion of guest atoms does not change the lattice structure of the host and is usually highly mobile [86]. Intercalation reaction involves separating 2D layers and the addition of guest molecules. This process requires enough chemical driving force between host material layers and intercalants [89]. The thermodynamic principle for intercalation reactions is shown in equation (4). It is important to note that the energy involved in the process is affected by changes in the chemical structure and electrostatic states, the lateral size of the exposed boundaries, and the mechanics of the layered structures [90]

$$2\Delta G_f$$
 (layer-intercalants) $-\Delta G_f$ (layer-layer) <0. (4)

For intercalation to happen in layered solids, the host layer and guest intercalants' energy levels or electron shells must match, which is controlled by the chemical structure. Three primary layered materials exist; graphite-like material dominated by Van der Waals gaps, TMD-like layered solids with polar covalent bonds and weak Van der Waals forces, and clay-like layered materials with high electron-negative elements on the surface. The (-O/-OH/-F) surface groups in clays exhibit high polarity, differentiating the intercalation method. MXenes have the following unique intercalation mechanisms: (i) The higher the polarity of the molecules, the more spontaneous the reaction (e.g. intercalation with

dimethyl sulfoxide), (ii) When cations with high solvation enthalpy are inserted, it enables the co-intercalation of solvents as the ions would dissolve in the solvent (iii) electrically polarized MXene nanosheets aid in the electrochemical intercalation of ions species which is the mechanism for energy storage [86]. Figure 7 shows an example of the clay-like structure MXenes also displays [70].

These clay-like properties of MXenes allow flexible, free-standing films to be produced, molded and dried into conducting objects in any shape or conductive coating on a surface to be painted after dilution. Figure 7(b) and (c) depicts the cross-section and top view of the clay-like MXenes. After hydration, the dried samples swell and shrink after drying. Figure 7(d) shows the MXenes molded into the letter M and dried to form a conductive solid [70]. The intercalations usually occur as electrostatic interactions and coordination interactions with metal cations. MXenes have the exact intercalation mechanism as layered clay minerals based on similar layer rigidity and surface terminations. However, the layers in MXenes are fused more tightly, requiring stronger chemical interactions to drive the intercalation process [86].

3.2. Effect of the different valence charges of vanadium carbide MXenes

Initially, non-stoichiometric and stoichiometric VC were investigated due to differences observed in mechanical and thermal properties, including high thermal and electric conductivity, high melting point, and high-temperature, high-temperature hardness, and corrosion resistance [73, 74]. Some applications include corrosion protection and binders, microelectronics, thermal barriers, catalysts, and functional coatings [85]. Chong et al investigated the stability of V₂C, V₄C₃, V₆C₅, and V₈C₇. It was observed that the stability of the VC compounds could be predicted from cohesive energies, formation enthalpies, and C vacancy in the crystal structure. The more negative the formation enthalpies of the VC compounds, the more stable the compound. Also, the C vacancy in the crystal structure of VC decreased the compound's stability. The formation energies calculated in this study were -0.541, -0.522, -0.466, -0.405 and -0.324 for V_6C_5 , V_8C_7 , V_2C , VC, V₄C₃ respectively. Therefore, the order of decreasing stability for the carbides was determined to be, $V_6C_5 > V_8C_7$ $> V_2C > VC > V_4C_3$ [91]. These findings indicate that V₆C₅ is the least reactive in the environment and retains its useful properties better than the other binary compounds. This result was also confirmed by Wang et al and Sun et al [85, 92]. As illustrated previously (figure 6(b)), the density of states (DOS) structure of VC, V_4C_3 , and V_8C_7 all have similar DOS structures with electronic core structures due to the C2p and V3d in -16 and -8 eV [85]. However, many atoms in the V₈C₇ unit cell resulted in higher DOS values. Also, all VC are considered metallic compounds because of their finite TDOS at the Fermi level [91]. The bonding between the metal (d) and non-metal (p) electrons results in

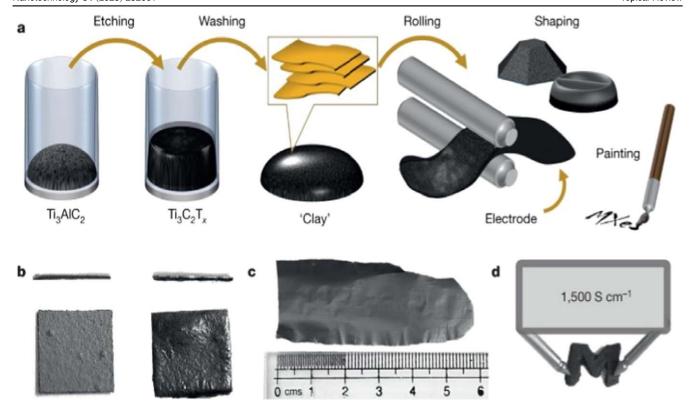


Figure 7. Clay-like structure of MXenes. Reproduced from [70], with permission from Springer Nature.

shear-resistive covalent bonding, which gives the VC compound its hardness [93].

3.3. Effect of interlayer spacing and functionalization of vanadium carbide MXenes in energy storage devices

2D layered materials generally can host cations of different sizes. This phenomenon is described as intercalation, the alterable exsiccation or embedding of a molecule or ion into the interlayers of layered structures [3, 94]. The intercalation mechanism became popular through first-generation lithiumion batteries (LIBs). It is essential to note that the etching method determines the interlayer spacing [95]. Wu et al reported that etching with fluoride salt (NaF) and HCl and HF yields a c lattice parameter (c-LP) of 22.0 Å and 19.8 Å respectively. [33]. Furthermore, the distance between MXene layers is closely linked to the number of intercalated water molecules. MXenes etched with HCl, and LiF (cations and water intercalated) are about 2.8 Å larger than the 50% HFetched MXene because of a layer of water and cations between the MXene layers in the previous case [96]. Controlling the interlayer spacing of MXenes and maximizing its use in energy storage applications, purification, and biomedical engineering can be achieved through cation intercalation. Understanding the intercalation's structural effects helps discover the best conditions for intercalating large cations, as large cations generally decrease the specific capacitance because of a void created in the electrode. Therefore, there is a trade-off between larger interlayer spacing and increased capacitance depending on the application of the MXene [3]. In a bid to improve the interlayer spacing and electrochemical performance of V₂C MXene by Liu et al, the MXene was first lithiated, which improved the peaks from $2\theta = 8.14^{\circ}$ to $2\theta = 8.03^{\circ}$. When tested, the prelithiated MXene demonstrated a higher specific capacity and reduced Li⁺ ions during SEI formation. Figure 8(a) shows the schematic of the working conditions of the MXenes before and after prelithiation, demonstrating that prelithiation can increase the MXene interlayers and recompense the Li loss in the initial cycle leading to a high reversible capacity [97]. Another study by Naguib et al revealed that upon mixing of V₂CT_x with -TBAOH for two hours, a peak shift from 2θ of 8.9° to 4.6° (c-LP from 19.9 Å to 38.6 Å) was observed. The total space increase was \sim 9.4 Å. Also, treatment of V_2CT_x with 50% aqueous choline hydroxide and n-butylamine resulted in c-LP of 36.0 Å and 36.3 Å [67]. To achieve a high-capacity rechargeable aluminum electrode, the V₂CT_r was also treated with TBAOH, which led to a 5.73 Å increase in the c-LP and was delaminated with NMP, a famous intercalation material for 2D structures. Figure 8(b) shows the XRD patterns of V_2CT_x treated with TBAOH and V_2CT_x without treatment which shows a 5.73 Å increase in the interlayer spacing and, ultimately, an increase in the specific capacity [59]. Another material intercalated with V_2CT_x was Sn. Herein, V_2CT_x was immersed in 2 M KOH at 40°C for 1 d and then transferred to 0.2 M stannic chloride at 40°C for 2 more days. V₂C@Sn was obtained after washing and freeze-drying. The XRD results show an enlarged c-LP of about 19 Å, indicating increased interlayer spacing using Sn as an intercalant. This expanded interlayer led to the synthesis of a material producing a

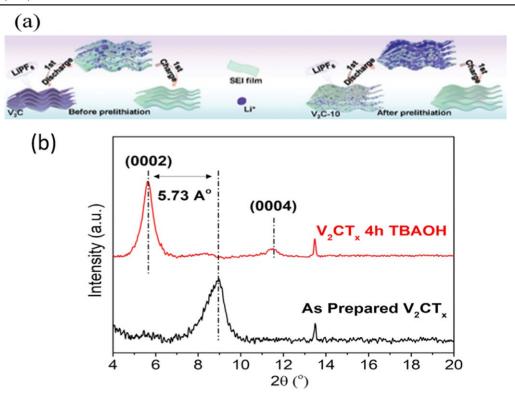


Figure 8. (a) Schematic of the working conditions of the MXenes before and after prelithiation Adapted from [97] with permission from WILEY-VCH, copyright 2020. (b): XRD Patterns of V_2CT_x Treated with TBAOH And V_2CT_x Without Treatment Reprinted (adapted) with permission from [59]. Copyright (2017) American Chemical Society.

coulombic efficiency of 96% and a high discharge capacity of 941 mAh g⁻¹ at 0.3 A g⁻¹ current density [98]. Also, Sn's valence change being reversible contributed to the LIB capacity and stability.

4. Vanadium carbide MXene application in energy storage devices

The emission of greenhouse gases and the strive to save the planet have led many companies to invest in developing more sustainable energy sources, thereby reducing the heavy dependence on fossil fuels [99, 100]. Renewable energy sources such as wind, solar and tidal energy offer an attractive alternative to fossil fuel because they reduce environmental pollution, improve economic development by providing job opportunities, and lower electricity costs, especially in rural, underdeveloped areas [101, 102]. However, energy generation from these sources is limited by weather inconsistencies and climate changes resulting in erratic power production. Therefore, energy storage devices are essential for storing and harvesting energy from different natural resources and conversion into electrical energy for on-demand use [103]. MXene-based materials for energy storage devices are integral in integrating high power, high energy, and long-term features into renewable energy devices [103]. Generally, MXenes with low formula weights, like Ti₂C, Nb₂C, V₂C, and Sc₂C, have demonstrated better gravimetric capacities than their higher-weight counterparts [103]. To this end, M_2X electrodes are expected to demonstrate better gravimetric capacities than M_3X_2 and M_4X_3 [104]. The current order of MXenes specific capacity is $Ti_2C < Nb_2C < V_2C$, indicating that vanadium carbide MXenes have the highest specific capacity[47]. This correlates with previous research, which estimated the theoretical capacity of V_2C as 940 mAh g^{-1} [105]. Materials with high specific capacity allow for energy storage devices with improved storage capacity to be synthesized. The high specific capacity of vanadium-based MXenes was illustrated by Zhou *et al*, where V_4C_3 was used as the anode material that could provide a high specific capacity of 225 mAh g^{-1} after 300 charge–discharge cycles [54].

4.1. Vanadium carbide MXenes in batteries

4.1.1. Vanadium carbide MXenes in Li-ion batteries. The development and application of LIBs in electric vehicles and portable electronics have reduced the dependence on fossil fuels due to the large energy density of LIBs [106]. It is no surprise that MXenes have entered the race as a formidable competitor because it improves LIBs and promises successful growth into batteries other than Li-based batteries [107]. The performance of Li batteries can be enhanced using MXene with different functionalization, formula weight, and type. The functionalization of MXenes affects its overall character, where research has shown that non-functionalized MXene displays magnetic properties while functionalized MXenes are semi-conductive [107]. In general, the surface

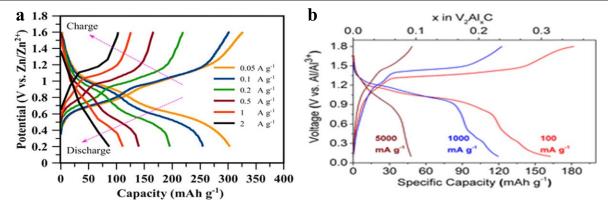


Figure 9. (a) Charge–discharge profiles of $V_2O_x@V_2CT_x$ from 0.05 and 2 A g⁻¹. Reprinted (adapted) with permission from [111]. Copyright (2020) American Chemical Society. [111] (b) charge–discharge profiles of the FL- V_2CT_x at different current densities in aluminum batteries. Reprinted (adapted) with permission from [59]. Copyright (2017) American Chemical Society.

terminations determine the performance of the MXenes with bare MXene. Oxygen terminations have higher capacity and excellent Li-ion transport instead of the hydroxyl and fluorine terminations, resulting in lower capacity and hindering Li-ion transport [47]. If the terminations are non-native, like Cl, an increase in the interlayer spacing occurs, and also, the adverse effects of the native OH and F functional groups are alleviated [107]. Functionalization also increases the interlayer spacing, thereby increasing Li uptake and transport. This is particularly important when using large ions of organic electrolyte (0.65-1.3 nm). These impede transportation between the MXene layers and limit the specific capacitance and rate capability [108]. This phenomenon was proven by Wang et al which dmonstrated that functionalizing vanadium carbide MXenes with atomic Sn⁴⁺ improves the Lithium-ion battery (LIB) battery performance and provides a reasonable rate and cycling stability [98]. This result was achieved by increasing the interlayer spacing of the MXene and the formation of the V-O-Sn bonds. An almost 100% reversible lithium storage capacity of 1262.9 mAh g⁻¹ was achieved after 90 cycles when the current density was 0.1 A g⁻¹. Comparing this result with Mashtalir et al shows a reduced capacity of 410 mAh g⁻¹ at a 1C cycling rate. This shows that to achieve the full MXene's full potential; an increased interlayer spacing is essential as it facilitates easy ion intercalation and storage, increasing the amount of energy a battery can store. Furthermore, studies by Yan et al illustrate that upon the decoration of V₂C with oxygen/sulfur, the resulting MXenes, after lithiation, remain metallic, lower the Li diffusion barrier, and increase their Li capacity, which validates their great potential alternative anodes [109].

4.1.2. Vanadium carbide MXenes in Non-Li batteries. There is no question that the massive development in the use of lithium-based energy storage devices might strain the world's lithium supply in the future. Hence, new chemistries of non-LIBs like Mg-ion, Al-ion, Na-ion, K-ion, and Ca-ion batteries have arisen as suitable substitutes in the next phase of sustainable energy technologies [84, 88–90]. As in Li-based batteries, vanadium-based MXenes promote the enhanced

performance of non-Li batteries offering increased interlayer spacing, which translates into better storage capacity. V_2CT_x demonstrated good cycling stability and high-rate capability when used as an anode in Na-ion batteries.

A study on charge storage mechanisms confirmed that the redox reaction at the transition metal (M) site in MXene is responsible for electrochemical storage [56]. Wei et al confirmed the high-rate capacity of V2CTx MXene intercalated with Mn²⁺ and tested in a sodium-ion battery was 425 mAh g⁻¹ at a current density of 0.005 A g⁻¹. This was due to the increased interlayer spacing provided by the intercalation of the Mn²⁺ [110]. It was also discovered that the Na⁺ storing capacity in V₂C@Mn is mainly capacitive with a linear relationship with current density and capacity [110]. Vanadium MXenes have also proven to be brilliant cathode materials in aqueous zinc-ion batteries, as shown by Venkatkarthick et al. Here, V₂CT_x, electrodes had enhanced capacities of 304 and 84 mA g⁻¹ at current densities ranging from 0.05 and 2 A g⁻¹, respectively [111]. The improved permeability, lower interfacial resistance for the electrolyte, good conductivity, and high surface areas correlate to V₂C high specific capacity [103, 112]. Figure 9(a) shows the charge-discharge profiles of V₂O_x@V₂CT_x. The figure shows that even at high current densities of 1 and 2 A g^{-1} , noticeable charge/discharge plateaus are noticed [111].

In aluminum batteries, V_2CT_x has proven to be an excellent cathode material even with the high charge density of Al^{3+} cations and its strong interactions with the host lattice [113, 114]. Vahid Mohammadi *et al*, V_2CT_x achieved specific capacities of 300 mAh g^{-1} at high discharge rates and discharge potentials. The V_2CT_x MXenes were pre-intercalated with TBAOH and then delaminated into single sheets, improving the batteries' interlayer spacing and, ultimately, specific capacity [59]. Figure 9(b) shows the charge–discharge profiles of V_2C in aluminum batteries. From the diagram, the electrodes displayed a high-rate capability. It also indicates that after charging at very high rates (1000 mA g^{-1}) and discharging at slower rates (100 mA g^{-1}) after 100 cycles, the cathode (intercalated MXene) could still produce a good

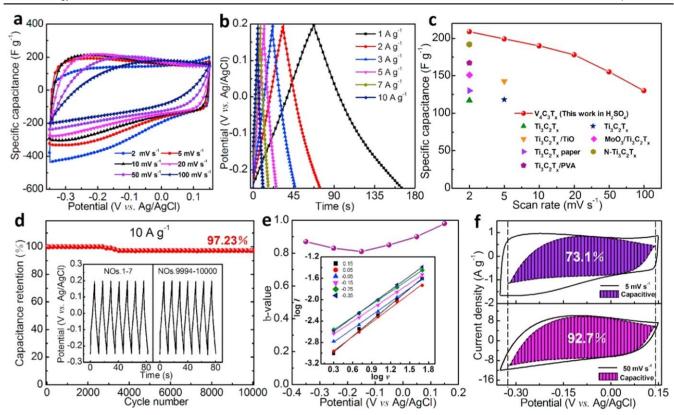


Figure 10. $V_4C_3T_x$ electrodes electrochemical performance in a 1 M H_2SO_4 electrolyte. (a) $V_4C_3T_x$ electrode CV curves at various scan rates. (b) The $V_4C_3T_x$ electrode's galvanostatic charge–discharge curves at various current densities ranging from 1 to 10 A g^{-1} . (c) The electrodes' gravimetric specific capacitance displayed as a function of scan rate. (d) The $V_4C_3T_x$ electrode's cycling performance at 10 A g^{-1} , with galvanostatic cycling data insets. (e) $V_4C_3T_x$ electrode *b*-values; inset plots log *I* versus log *v* (f) Capacitive contribution to total current at chosen scan rates as determined by CV partition analysis. Reprinted from [51] Copyright (2019), with permission from Elsevier.

discharge capacity of 76 mAh g⁻¹ and columbic efficiency of approximately 96.6% [59].

4.2. Vanadium carbide MXenes in supercapacitors

Supercapacitors have high power densities, longer operating life, more significant power, and high-power rates. Supercapacitors can also be included within a battery to improve the size while improving its power requirements and increasing the lifetime [1, 115]. The breakthrough for supercapacitors has been restricted due to the lack of cheap, stable, and highly efficient electrode materials with good conductivity. Some of the issues with the researched electrode materials include insufficient interlayer spacing, poor conductivity, and volume expansion [21, 116, 117]. MXenes, on the other hand, have proven to have larger interlayer spacing, quick ion diffusion, controllable structure and morphology, high surface area, and good electrical conductivity, which is a crucial factor in supercapacitors [1]. Wang et al study of vanadium carbide MXenes again illustrated high capacitance and retention rate when tested as supercapacitor electrodes. The research discovered that $V_4C_3T_x$ shows a high capacitance of 209 F g⁻¹ at 2 mV s⁻¹, good rate performance, and stable long cyclic performance with capacitance retention rate 97.23% after 10 000 cycles at 10 A g^{-1} in 1 M H_2SO_4 . This was due to the wide interlayer spacing, large specific surface area, good pore volumes, and excellent hydrophilicity [51].

Figure 10 shows the electrochemical performance of $V_4C_3T_x$ electrodes [51]. The cyclic voltammetry curves in figure 10(a) show that the charge and discharge capacitance differ between the given potential window. This is due to the irreversibly intercalated cations trapped during the discharge process between the $V_4C_3T_x$ layers [49]. Figure 10(b) shows GCD curves and cyclic performance at various current density between -0.25V and 0.2V (versus Ag/AgCl). The shapes obtained from the CV and GCD tests show that the $V_4C_3T_x$ electrodes exhibit typical capacitive behavior. Figure 10(c) proves that $V_4C_3T_x$ has a higher specific capacitance than previously reported Ti-based MXenes with a specific capacitance of 209 F g⁻¹. This result is proven in previous reports where Ti-based MXenes had a capacitance of 143 F g^{-1} [118], 117 F g⁻¹[119], 118 F g⁻¹ [120], and 192 F g^{-1} [121]. It confirms the inverse relationship between scan rate and capacitance [51]. As the gravimetric specific capacitance of the electrode decreases, there is an increase in the scan rate due to limited kinetics [51]. At gravimetric capacitance of 209, 199, 190, 178, 155, and 130 F g^{-1} , the scan rates were 2, 5, 10, 20, 50, and 100 mV s⁻¹, respectively [51]. From figure 10(d), the capacitance retention is 97.23% even after 10 000 cycles at 10 A g⁻¹ proving excellent capacitive behaviors. Figure 10(f) shows that scan speeds

Table 2. Capacitance of vanadium MXenes in energy storage devices.

Battery composition	Capacitance (mAh g ⁻¹)	Supercapacitor composition	Capacitance (F g ⁻¹)	References
Sn^{4+} functionalized $\operatorname{V_2CT}_x$ in Li-ion batteries	1262.9	Bare $V_4C_3T_x$	209	[51, 98]
Bare V_2CT_x in Li-ion batteries	410	Bare V_2CT_x	487	[49, 109]
Mn^{2+} functionalized $\mathrm{V_2CT}_x$ in Na-ion batteries	425	Bare $V_4C_3T_x$	330	[110, 123]
Bare V_2CT_x in Al-ion batteries	300	Bare V_2CT_x	181.1	[59, 124]
Bare V_2CT_x in Al-ion batteries		Bare $V_8C_7T_x$	161.7	[125]

below 50 mV s⁻¹ have little or no effect on the overall capacitance, demonstrating that redox processes are not diffusion-limited but classified as semi-diffusion-controlled processes [122]. Dall'Agnese *et al*, V_2CT_x was used as a cathode material in a sodium ion capacitor. An entire asymmetric cell was assembled using hard carbon as an anode material in their work. The cell achieved the capacity of 50 mAh g⁻¹ with a maximum cell voltage of 3.5 V. The results proved that V_2CT_x could be an attractive cathode material with a wide operating window.

Shan et al reported the electrochemical behavior of V₂C in three aqueous electrolytes: MgSO₄, H₂SO₄, and KOH. Exceptional specific capacitances were achieved, specifically 487 F g^{-1} in 1 M H₂SO₄, 225 F g^{-1} in 1 M MgSO₄, and 184 F g^{-1} in 1 M KOH. This work shows V₂C MXene as a promising electrode for energy storage using aqueous electrolytes [49]. Vanadium carbide (V₄C₃) MXenes were successfully synthesized by Syamsai et al through HF etching. Testing the electrochemical performance revealed the specific capacitance to be 330 F g⁻¹ at 5 mV s⁻¹ in 1 M H₂SO₄ electrolyte and a high retention rate of 90% even after 3000 cycles [123]. This result signifies the stability of V₄C₃ as an electrode and a decline in the charge storage capacity of 10% after charging and discharging 3000 times. Hongtian *et al* demonstrated the versatility of V₂CT_x as a supercapacitor electrode using seawater as the electrolyte. A capacitance of 181.1 F $\rm g^{-1}$, volumetric specific capacitance of 317.8 F cm⁻³, and an 89.1% capacitance retention after 5000 cycles were achieved[124]. A polycrystalline intermetallic vanadium carbide (V₈C₇) was effectively synthesized and tested as an electrode material for electrochemical capacitors by Zhang et al. The V₈C₇ electrode was tested in 1.0 M Na₂SO₄ at a specific current density of 1 A g⁻¹ and had a large specific capacitance of 161.7 F g⁻¹. The electrode retained 92.8% of the specific capacitance after 10 000 cycles. 83.3% of the initial capacitance was maintained even at a high current density of 10 A g^{-1} [125]. The large ionic radius of potassium makes it difficult for K⁺ ion capacitors to expand, even though the low cost of these materials makes it advantageous [117]. The results from this study indicated that materials with small interlayer spacing and open framework are unpromising for use in electrodes and would produce low capacitance. However, Ming et al tested V₂CT_x as a supercapacitor electrode. The device achieved a high energy density of 145 Wh kg⁻¹ at a power density of 112.6 W kg⁻¹, suggesting that K-V₂C can be promising electrodes in mobile ion capacitors [126].

To summarize, table 2 below shows a summary of vanadium Mxenes used as electrodes in supercapacitors and batteries.

5. Gaps in the current knowledge

Since the discovery of the first MXene, many questions are still left unanswered to maximize the capacity of MXenes fully. More than a hundred different MAX phase compositions have been predicted and studied, leaving a plethora of ternary carbides to be converted into MXenes. Any layered transition metal carbide or nitride with the formula $M_{n+1}X_n$ layers and separated with A-group metals can be etched into a MXene. Therefore, the synthesis of MXenes is a significant research direction. The HF synthesis method with the highest yield is LiF-HCl etching, which yields 91.3% [57]. However, other non-toxic methods like halogen etching of the vanadium MXenes should be implemented. In energy-storage applications, more work is required to minimize the first-cycle irreversibility and capacity drop observed after Li- and Na-ion intercalation. Also, an indepth understanding of the intercalation mechanism of multivalent and large organic ions would deliver essential strategies for emerging electrode materials for the next group of batteries and supercapacitors. Finally, another critical research path is the in-depth research on aligning the theoretical capacity of vanadium carbide MXenes with the practical, specific capacity. V₂C has a theoretically higher specific capacity in LIBs than all other MXenes. A deep understanding of the electrochemical energy storage mechanisms of MXenes, the pure synthesis procedure for vanadium MXenes, and the influence of the surface terminations would help to develop more useful electrodes.

Furthermore, using MXenes as flexible and transparent electrodes is extremely important for the next generation of consumer electronics. Also, the scale-up of MXene synthesis is crucial to take MXenes from the laboratory to the industry. Shuck *et al* developed a model that mitigates the safety concerns during MXene synthesis and increases the yield of the MXenes [127]. However, an in-depth understanding of the synthesis-structure-property relationship is required to scale-up MXene production. Lastly, there has been much research on titanium-based MXenes, but only a few on their vanadium counterparts. Hence more attempts at utilizing V_2C as a promising electrode should be investigated in both batteries and supercapacitors.

6. Conclusion

Developing improved electrode materials can meet the high need for electrochemical energy storage systems. The disadvantages of various electrode materials, such as carbon and its derivatives, metal oxides, and conducting polymers, have sparked interest in recent decades; therefore, new electrode materials are being investigated. This has led to the discovery of new 2D materials with separate layers in 2D. In 2011, a new 2D electrode material called MXene was studied. MXenes also have outstanding qualities such as brittleness, high melting point, oxidation resistance, high electrical and thermal conductivity, hydrophilic nature, compositional diversity, a wide surface area region, and a proclivity to support a wide range of intercalants. As a result, it was created as an alternative to the materials used in prior electrodes. The vanadium MXene, in particular, has a high theoretical capacity of about 940mAg⁻¹, making it a good candidate for synthesizing high-capacity energy storage devices. In this study, recent technologies for synthesizing 2D MXenes and their applications are discussed in this review with specificity in vanadium carbide MXenes.

However, the pure synthesis of V_2C is still an issue due to the low formation energy of V_2C in addition to the toxicity of the hydrofluoric acid synthesis process discussed. It can also be seen that V_2C has good excellent metallic conductivity; however, the fabrication of high energy density electrode materials is still pending to provide for the popularity of wearable and flexible devices. Also, storing these V_2C MXenes is a big issue due to the multivalent state of vanadium. However, it is advised that storage should be done in an oxygen-free low-temperature environment or dissolved in a polar solvent to reduce the degradation of the MXene. Lastly, the benefits of using vanadium MXene hybrids in improving the restacking issue MXenes face and the electronic conductivity, stability, and easy ion/electron transport is discussed. To this end, MXenes provide a promising starting point for future research into energy storage applications.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Ayomide Adeola Sijuade https://orcid.org/0000-0002-0147-019X

Vincent Obiozo Eze https://orcid.org/0000-0003-1484-2922 Okenwa I Okoli https://orcid.org/0000-0003-1918-6442

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