Perispective

MXene for high energy and power density: a perspective

Chengxiang Wang, Xianfen Wang, Luyuan Zhang and Longwei Yin

1 Key Laboratory for Liquid–Solid Structural Evolution and Processing of Materials, Ministry of Education, School of Materials Science and Engineering, Shandong University, Jinan 250061 People’s Republic of China
2 Institute of Materials for Energy and Environment, College of Materials Science and Engineering, Qingdao University, Qingdao 266071 People’s Republic of China
E-mail: wcxmat@sdu.edu.cn and yinlw@sdu.edu.cn

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Abstract

MXenes as a family of unique 2D materials with high conductivity, atomic thickness, redoxable property and plenty of surface groups have been extensively explored for energy storage. Energy and power densities are always increasing along with the development of controllable synthesis, surface chemical groups and microstructure regulations. Herein, we reviewed present progresses in MXene-based materials for high performance energy storage. Specific discussion was focused on novel structure design, surface group regulation and multivalent ion battery applications. Finally, based on the aforementioned results and discussions, personal perspectives on the MXenes for high energy and power are presented.

1. Introduction

MAX phase is a family of non-van-der-Waals-type layered compounds with the formula of M_{n+1}AX_n (n = 1, 2, 3, M = transition metal, A = main group elements, X = C/N) [1, 2] (figure 1). It is composed of MX slabs (consist of covalent-bonded M₆X octahedral) with a pure group A element layer in the galleries, with one layer of M₆X octahedral for n = 1, two layers for n = 2, and three layers for n = 3, as shown in figure 1. They are famous as metallic ceramics with the advantage of high thermal and electrical conductivity, excellent resistance to thermal shock, corrosion and oxidation, etc. MXenes are a group of 2D materials with unique nanosheets through delaminating MAX phase, for which A was removed by etching, leaving stacked MX sheets that can be exfoliated to single layer or few-layers. Usually, MXenes’ surface is terminated with functional groups of –O, –F and –OH, which are undesirable for energy storage but inevitable after delamination and exfoliation. Due to the high conductivity, 2D MXenes are excellent conductive supporters for active materials. Importantly, MXenes are electrochemically active and redoxable for metal ion. Therefore, MXenes have been intensively investigated as structural supporter and working electrode material. Till now, MXenes have been widely employed in energy storage applications [3–5], including metal ion batteries (Li⁺, Na⁺, K⁺, Mg²⁺, etc) [6–11], supercapacitors [12, 13], Li–O₂ batteries [14].

High energy and power density are the significant goals for the energy storage devices. Novel materials design is a promising way in addressing the aforementioned goals. MXenes possess lots of unique features, such as molecule-level thickness, high conductivity, redoxable activity and fruitful functional groups, which are beneficial to the enhanced energy storage performance. Here, we focused on recent progress concerning on the enhanced capacity and power performance for MXene-based electrodes. The promising strategies including electrode structure design, surface group regulation and multivalent ion battery application are summarized, highlighting the microscale design on the component orderliness, controllable synthesis and surface groups of MXenes.

2. Electrode structure design

2.1. Heterostructures

Fast ion/electron transport rates are of great significance for high energy and power. Heterostructures composed of nanosheets are sophisticated for efficient ion diffusion and electron transfer. Usually,
heterostructures are composed of the conductive matrix and the redoxable nanosheets. MXene-based heterostructures like MXene/graphene [15, 16], MXene/phosphorene [17, 18], MXene/layered double hydroxide (LDH) [19], MXene/transition metal dichalcogenide (TMD) [20], have been reported. These heterostructures demonstrate the following advantages [19]: (1) the molecular-level thickness drive the active sites onto the surfaces; (2) Electrons could transport from the MXenes sheets to the active layers through the neighboring sheets, allowing the electron transfer to the active materials; (3) the unique 2D ion diffusion channel size can be tuned artificially for rapid ion diffusion. Efficient ion/electron transport definitely leads to a higher material utilization ratio. For example, MXene/graphene heterostructures delivered a reversible capacity of ~340 and ~180 mAh g\(^{-1}\) at the high current rates of 1 C and 10 C, respectively, and a capacity of ~220 mAh g\(^{-1}\) was maintained at 2.5 C after 100 cycles [21]. The performance of heterostructures surpassed those of pure MXene and rGO films [21]. The heterostructure designing strategies well meet the demand of supercapacitors which pursuit the high energy density at high rate charge/discharge. MXene/LDH heterostructures deliver a higher energy density than those of pure LDH nanosheets and rGO/LDH heterostructures. As shown in figures 2(a)–(b), Bode plots of Co-Al LDH/rGO heterostructure indicated a knee frequency at ca.100 Hz, which is almost equivalent with rGO-based EDL capacitors. But this value of Co–Al LDH is only several Hz [22]. Similarly, Ti\(_3\)C\(_2\) could improve the knee frequency of NiCoAl–LDH from 0.5 Hz to 2 Hz [19]. This proved that electrons in the heterostructures work in a more efficient way. Electrons into/out of redoxable LDH nanosheets can be collected on the adjacent MXene/rGO nanosheets and efficiently transported to outside circuit, significantly raising the capacitive charging and discharging ability. More importantly, nanosheet heterostructures exhibit a larger specific capacitance than the physical mixed nanosheets [19, 22]. This evidently highlights the significance of designing ordered structures as electrodes for enhanced performance [23].

It was predicted that heterostructure of 2D materials have an interfacial charge transfer and a strong electronic coupling effect at the heterointerface [24–26]. Heterostructures with MXenes usually display obvious synergetic effect on the physicochemical properties such as ion adsorption energy, ion diffusion barrier, etc. MXene/phosphorene heterostructures enhanced the adsorption and intercalation of Na atoms. The binding energy of Na on black phosphorene (BP)/Ti\(_3\)C\(_2\) system was ~ −2.83 eV, which is much lower than that of Na on the pristine BP (~ −2.17 eV) (figure 2(c)). It seems that Na ions prefer to adsorb on the BP nanoparticle anchored on Ti\(_3\)C\(_2\) matrix, suggesting the strong interaction between BP and Ti\(_3\)C\(_2\) nanosheets [17]. However, the question is lower adsorption energy also means larger desorption barrier, which is bad for the charging process. How to define the roles of adsorption energy is a common question for those to take it to assess the effect of heterostructure, and this has not been well answered. Bader charge calculations (figures 2(d)–(e)) indicated Ti\(_3\)C\(_2\) changes the charge density profiles around Na and P. The Valence state of most P atoms from Ti\(_3\)C\(_2\)/BP heterostructures in the discharging process was more than −0.5, while the value for pristine BP was only ca. −0.2. This implies that Ti\(_3\)C\(_2\) nanosheets can evidently change the
sodiation state of BP nanoparticles, making it easier to get electrons from Na and facilitate the sodiation process. The ion diffusion behavior was also enhanced for heterostructures compared with the pristine monolayer [18, 27, 28]. The diffusion barrier depended on lot of parameters, such as surface groups, ion species and nanosheet types. The diffusion barrier of Na atom along both outside path in BP/Ti$_3$C$_2$(OH)$_2$ and BP/Ti$_3$C$_2$F$_2$ are lower than that along the monolayer BP, Ti$_3$C$_2$(OH)$_2$, and Ti$_3$C$_2$F$_2$. Ti$_3$C$_2$F$_2$ was more efficient than Ti$_3$C$_2$(OH)$_2$ in decreasing Na diffusion barrier when Na ions diffuse in the interlayer of Ti$_3$C$_2$/BP heterostructures [18]. The diffusion of Na, K, and Ca ions on MXene/graphene heterostructures (MXene = Sc$_2$C(OH)$_2$, Ti$_2$CO$_2$, or V$_2$CO$_2$) also have been systematically investigated using first-principles methods by Demiroglu and co-workers [28]. Diffusion energy barrier of MXene/graphene heterostructures are half of that for MXene system. Ti$_2$CO$_2$/graphene and V$_2$CO$_2$/graphene systems have similar diffusion energy barriers. K and Na ions show the barrier of 0.26 and 0.34 eV in the heterostructure system. This is comparable with, or even lower than Li$^+$ in the same system (0.22–0.6 eV) [29], on graphite (0.5 eV) [30], although the diameter of Na$^+$ and K$^+$ is much larger than Li$^+$.

Although heterostructures with 2D materials was reported to have an enhanced performance, the underlying mechanism is still unclear. The calculation results seem not better than the phenomenological model, such as the close contact and large contact area to ensure effective electron transfer, 2D interlayer to enable fast ion diffusion. Now, direct experimental evidences are absent to confirm the predicted synergetic effect, including the binding energy and diffusion barrier of MXene. It is urgently required to investigate the heterostructure-based batteries in a precise way as the FET. In-situ characterizations are necessary to resolve such issues. Nevertheless, designing the microscopic orderliness like heterostructures for energy storage would be a promising way to achieve high energy and power.

2.2. In-situ growth of guest materials

MXenes were used as ideal conductive supporter because it is conductive, flexible, redoxable and surface group adjustable. The alloying-type anodes have been suffered from the huge volume change and low conductivity, leading to poor cycle stability and low capacity. Designing nanoscale anode materials on a conductive matrix is an effective way to address the above problems. 2D materials have also been widely used as supporting matrix for Si, P, Sn, or related compounds. However, the challenge is how to achieve the uniform, monodispersed and nanoscale particles onto MXenes surface, preventing the aggregation and peeling-off of as-prepared nanoparticles in the charge–discharge process.
Free-standing nanomembranes possess the large surface area, which is suitable for stable interfacial reactions, e.g. molecule/ions adsorption/desorption [31]. As nanomembranes, MXenes surfaces are negatively-charged and covered by varieties of surface groups, providing controllable sites in synthesizing uniform particles on the surface. The surface groups like –OH, –F or –O could serve as anchoring points for in-situ nucleation and growth of uniform particles through hydrolysis [32] or reduction [33, 34]. According to MXenes in exfoliated or un-exfoliated state, there are different requirements on synthesis procedure.

To removing ‘A’ from MAX phase without sonication for un-exfoliated MXenes, it is usually required to insert/adsorb the precursor cations like metal ions or metal-organic ions to further expand the MXenes interlayer. All of these ions are too huge to intercalate into the interlayer of MXenes, either with hydration shell or long organic chains. Cationic surfactants like dodecyltrimethylammonium bromide (DTAB), cetyltrimethylammonium bromide (CTAB) and stearyltrimethylammonium bromide (STAB), etc [35], and ammines like odecylamine (DDA [36]) and ammonia hydrate [34] have been reported to further tune the interlayer distance of MXenes successfully. Cationic surfactants could intercalate into the interlayer of negatively charged Ti$_3$C$_2$ via the electrostatic interaction (figure 2(a)), replacing H$^+$ in the [Ti–O]–H$^+$ with [Ti–O]–CTA$^+$ (CTAB for example). The CTA$^+$ ion is substitutable by sequential metal ions such as Sn$^{4+}$ to form [Ti–O]–Sn$^{4+}$, which could be reduced to the uniform Sn nanoparticle (2–5 nm, figure 2(b)) in-situ accommodating in between the MXenes interlayers [35]. In this process, sufficient precursor dosage could lead to the formation of nanolayers rather than nanoparticles [34].

For exfoliated MXenes, it formed metastable suspension of nanosheets. Direct adding metal ions into MXenes solution will lead to the flocculation and gelation. This could be attributed to the strong interaction between the ions and –OH groups on the MXenes surface. Interestingly, cations with +2 or +3 valence state was helpful to make hydrogel, but univalent K$^+$ ions only lead to coagulation [37]. In fact, we can further decorate the formed 3D MXenes network through in-situ growth of active materials. The surface groups still exist after forming flocculation or hydrogel, which could be used for in-situ deposition of active material. Bimetallic phosphide nanoparticles NiCoP was prepared on Na$^+$ -flocculated 3D Ti$_3$C$_2$ wrinkled architectures through the in-situ hydrolysis of Ni$^{2+}$ and Co$^{2+}$ adsorbed on Ti$_3$C$_2$ surface groups, forming uniform nanoparticles with 10–20 nm diameters [38].

Further restriction conditions could be introduced to control the diameter of in-situ growth of active materials on MXenes. The surfactant-assistant method could be taken to control the species size further. CTAB with hydrophilic and hydrophobic groups was absorbed onto the surface of Ti$_3$C$_2$ via electrostatic interaction. This could separate a thin hydrophilic region on the Ti$_3$C$_2$ surface (figure 2(c)) from the aqueous solution, and control the size of prepared particles via tuning the dosage of water in sequential hydrolysis reaction (figure 2(d)) [39].

The surface groups can induce in-situ growth of guest materials and the uniform deposition of nanoparticles on MXenes with improved specific capacity and rate performance. This method is suitable for the controlled deposition of active materials on MXenes through ion hydrolysis. But there is no clear model to reveal the mechanism. The most impressive fact is that the composite electrodes exhibit a long cycle stability after solving with the problem of volume expansion and pulverization. Consequently, GeO$_2$@MXene showed a high-capacity retention of $\sim$1048.1 mAh g$^{-1}$ at 0.5 C after 500 cycles with the Coulombic efficiency (CE) of 99.8% [34]. MXenes/Si@SiO$_2$@C exhibited 99.69% CE after 1000 cycles at 10 C [40]. This can be attributed to following reasons: (1) The MXenes layers construct 2D confined spaces to restrict the movement and escape of anode materials, and they can expand freely in a certain range perpendicular to the surface to accommodate the isotropic expansion; (2) The chemical bonds between the active materials and MXenes could protect the active nanoparticles from escape and aggregation in the charge–discharge process.

2.3. Low-tortuosity electrodes

The prevalent strategies for improving the ion diffusion rate include expanding the interlayer and introducing pores into 2D materials, which decreases the electrode packing density and volume energy density. For 2D materials electrode, the large film thickness of industrial standard $>100 \mu m$ leads to a serious performance degradation [41]. The tortuosity of ion diffusion channels plays a significant role in this process from both theoretical and experimental view point [42]. Low-tortuosity electrodes with vertical alignment of 2D materials enable direct ion transport, leading to the thickness-independent electrochemical performance in thick films (figures 4(a)–(b)) [43]. The critical point is how to align 2D materials vertically on the substrate in a large area. There are two strategies now to prepare such vertical alignment 2D materials, (1) mechanical cutting process, (2) mechanical shearing of a discotic lamellar liquid-crystal phase.

Yoon and co-workers innovated a simple hand-rolling and cutting processes to prepare vertically aligned rGO (VARGO) film on substrate (figure 4(f)) [43]. It has an open edge structure and low-tortuosity ion diffusion channel with high packing density of 1.18 g cm$^{-3}$. A very high volumetric capacitance of 171 F cm$^{-3}$ and areal capacitance of 1.83 F cm$^{-2}$ in 6.0 M KOH electrolyte were obtained. Similar
mechanical cutting method has been applied to prepare hierarchical vertically aligned MXene arrays, which can avoid the MXenes restacking and facilitate the ion migration [44]. The MXenes arrays exhibited a higher volumetric capacitance of 485 F cm$^{-3}$ at 1 A cm$^{-3}$, due to the redoxable nature of MXene. More importantly, the high capacitance was partially maintained when the thickness of active materials increased. Xia and co-workers prepared vertically aligned MXene by mechanical shearing of a discotic lamellar liquid-crystal phase of Ti$_3$C$_2$Tx [41]. The non-ionic surfactant, hexaethylene glycol monododecylether (C$_{12}$E$_6$), was taken to enhance molecular interactions between the nanosheets and improve the packing symmetry (figure 4(c)). An external mechanical shearing force was imposed to align a higher-order discotic lamellar phase vertically, which is attributed to torque arising from flow-induced fluctuation in the lamellar or smectic phase (figures 4(d)–(e)). The electrode is extremely stable, maintaining almost 100% of the capacitance after 20 000 cycles at 20 A g$^{-1}$. For the 200 µm thick film, more than 0.6 F cm$^{-2}$ capacitance is maintained at the scan rate up to 2000 mV s$^{-1}$. The capacitance is almost thickness-independent, which is about the same for mass loading 2.80–6.16 mg cm$^{-2}$ at scan rate in the range of 1000–2000 mV s$^{-1}$. This result shows the possibility of charging/discharging thick-film electrode at very high rates, both for supercapacitors and batteries.

Obviously, lowering the tortuosity is effective to enhance the rate performance even at a high mass loading. Especially, mechanical cutting process is an easily-operated and scalable technique to prepare low-tortuosity electrode, which is promising for industrial production. Low tortuosity strategy is very attractive for fast charging of Li ion battery, which is one of the concerns of electric vehicle. However, present electrodes are composed of pristine rGO or MXenes, which specific capacity is much lower than that of alloying-type materials. It is quite fascinating to incorporate alloying-type anode material in such lower tortuosity electrode to realize fast charging and high capacity.

2.4. Surface group regulation

MXene surfaces are terminated with plenty of functional groups (–OH, –F and –O), which are randomly distributed on the surface of Ti$_3$C$_2$X and prefer to stay on the top sites of the Ti(c) atoms in the Ti$_3$C$_2$ monolayer [45]. The surface groups play an important role to determine the energy storage performance of MXenes. The bared surface and MXenes with –O are suitable for high performance, while MXenes with –OH and –F terminals are not. Both experimental and calculation results demonstrate that –OH groups could passivate the MXene surfaces undesirable for intercalation and adsorption of ions [46]. Additionally, the terminals of –OH and –F show steric effects to impede the spatial occupancy of ions, leading to a lower capacity [47]. In contrast, O-terminated would involve in electrochemical reactions for improved energy storage. The proportion of –O groups was reported to determine the capacitance of MXene [48]. On the other hand, MXenes with bared surface exhibit even higher capacities and rate capabilities than O-terminated ones [49].
Surface functional groups are changeable through chemical or physical methods, which could greatly improve the performance of MXenes. The F groups could be replaced by oxygen-containing groups, such as \(-\text{OH}, -\text{OOH} \) and \(-\text{O}\) \([50]\), when MXenes were immersed into the basic solution because Ti–F bonds are unstable in the basic environment \([46]\). KOH-treated Ti\(_3\)C\(_2\)T\(_x\) exhibits a higher gravimetric capacitance due to oxygen-containing groups induced pseudocapacitive behavior \([50]\). In fact, \(-\text{O}\) groups are more favorable than \(-\text{OH}\) according to aforementioned description, especially for battery applications. Besides, there are other effective processes to turn \(-\text{F}\) or \(-\text{OH}\) groups to \(-\text{O}\) groups on MXenes: (1) annealing treatment under vacuum or inert atmosphere (figure 5(a)) \([46, 51]\), (2) N-Butyllithium treatment (figure 5(b)) \([52]\). Ti\(_3\)C\(_2\)T\(_x\) annealed in Ar exhibited three times higher capacitance than the pristine MXenes, due to the fewer \(-\text{F}\) groups and larger interlayer distance \([51]\). The problem for annealing MXenes is the easy oxidation even with inert gas protection. Chen and co-workers took a novel n-butyllithium-treated method to turn the \(-\text{F}\) and \(-\text{OH}\) terminal groups to \(-\text{O}\) groups. Since \(-\text{OH}\) and \(-\text{X} \) (X=halogen) groups could turn to ether groups in strong nucleophilic reagent for the organic reactions \([52]\). Compared with the traditional alcalization treatment method, the n-BuLi-modified Ti\(_3\)C\(_2\)T\(_x\) MXenes own more \(-\text{O}\) and less \(-\text{F}\) terminal groups without damaging the two-dimensional structures (figure 5(c)). The n-BuLi-treated Ti\(_3\)C\(_2\)T\(_x\) achieved an excellent capacitance of 523 F g\(^{-1}\) at 2 mV s\(^{-1}\), and this is the highest value reported for the surface-modified MXenes in 1 M H\(_2\)SO\(_4\) electrolyte. At the same time, only a limited increase of the capacitance of the LiOH-treated Ti\(_3\)C\(_2\)T\(_x\) was observed with 259 F g\(^{-1}\) at 2 mV s\(^{-1}\).

The adsorption and diffusion of ions on MXenes has been revealed to closely relate with surface groups \([46]\). For \(-\text{OH}\) terminated MXene monolayer, only two Li atoms — one on either side — could adsorbed on a
2 × 2 unit. In contrast, –O terminated MXenes monolayers show a surprising eight-four on either side-Li atoms adsorption on a 2 × 2 unit, comparable for that of bare MXenes. The extra Li layers are actually adsorbed on the pre-lithiated MXenes, which has the same adsorption energy (E\text{ad}) for extra Li layers. For example, −1.552, −1.541, −1.592, and −1.554 eV per Li atom were calculated for Ti\text{C}\text{O}\text{Li}_2, V\text{C}\text{O}\text{Li}_2, Nb\text{C}\text{O}\text{Li}_2, and Ti_3C_2\text{OLi}_2, respectively, for the extra Li layer (2 extra Li per MXene unit). The E\text{ad} of extra Li atoms are similar for all MXene species, also comparable to those on graphene (−0.934 to −1.598 eV atom\textsuperscript{−1}) [53, 54], slightly higher than the bulk Li cohesive energy, suggesting that Li could adsorb several layers on top of the lithiated MXenes surfaces (figure 5(d)). Two extra Li atom layers can adsorb onto MXenes’ surface before a bulk-like arrangement become favorable, i.e. the capacity could potentially be tripled, suggesting a potential large capacity of MXenes. Valence electron localization functions (ELF) of (110) sections (figures 5(e)–(f)) revealed the formation of the negative electron cloud with the extra Li layers, demonstrating the strong interaction between different Li layers. It suggests the extra Li layer is able to bind with the lithiated MXenes. This is different from pristine graphene, where E\text{ad} falls rapidly to the bulk Li cohesive energy after an extra Li layer is attached [55, 56]. To explore the capacity of multilayer adsorption, a large space is needed to accommodate Li ions. Therefore, the exfoliated Ti\text{C}\text{C}_2 has a capacity of 410 mAh g\textsuperscript{−1}, 4 times higher than that of un-exfoliated Ti\text{C}\text{C}_2 (100 mAh g\textsuperscript{−1}), because of the larger surface [46]. Wang and co-workers have observed double layer adsorption of Na atoms within Ti\text{C}\text{C}_2 X interlayer through STEM. The multilayer adsorption of Li atoms and the effect of –O groups still need to be proved. 

So far, it is no doubt that –O and bare surface is conductive to achieve high energy and power density of MXenes. However, mild treatment method is scarce, and few experiments were reported to provide the bare surface. Inhibiting surface groups (especially F) in preparation should be better than the post-treatment. F-free agents and nonaqueous solvent could be ideal for this purpose [57]. On the other hand, surface groups can functionalize MXenes with tunable surface. Functional groups including redoxable, structure-directing or conductive moieties could be grafted to the MXenes surface, further enhancing the electrochemical performance.
3. Multivalent ion batteries

Multivalent ions, such as Mg\(^{2+}\), Al\(^{3+}\) and Ca\(^{2+}\), have attracted increasing attention due to their advantages in cost, energy density and safety for large scale energy storage devices. However, transitional intercalation-type graphene anode is not suitable for the application due to the relatively large diameters. Intriguingly, MXenes were demonstrated to be able to accommodate Mg\(^{2+}\), and Al\(^{3+}\) ions within the interlayer when used for pseudocapacitors \([58]\).

The storage behavior of multivalent ions of MXenes has been systematically investigated through calculation \([49]\). On the O-terminated MXenes, Al can only form partially chemisorbed first layer due to the positive adsorption energy, while Mg and Ca give a full monolayer coverage of MXenes with negative adsorption energy. The trivalent Al atom donate more electrons to fulfill the O bands than the divalent Mg and Ca. Thus fewer Al was needed, and further adding Al atoms cause an instable Al adsorption layer. In accordance with the coverage, Al, Mg, Ca show a high capacity of 552, 570, and 487 mAh g\(^{-1}\), respectively, in Ti\(_2\)CO\(_2\) MXenes. This is much higher than the monovalent Na (288 mAh g\(^{-1}\)) and K (264 mAh g\(^{-1}\)).

Multivalent ions can also form a multilayer adsorption on O-terminated MXene, which is useful to achieve a large capacity. Mg was demonstrated to have a stable second-layer adsorption on the top of the first magnesiated layer, while Ca only forms a partial second layer. ELF revealed that electrons for Mg spread out in the metal layers forming a negative electron cloud (NEC), which can screen the repulsion between the positive metal ions (adatom-adatom, adatom-Ti) and stabilize the second-layer adsorption. However, in the case of Ca, the electrons are more localized with weaker screening effects. As mentioned before, the adsorption behavior was influenced by surface groups. On bare MXenes’ surface, Al and Mg can form up to three adsorption layers, corresponding to 1488 and 1050 mAh g\(^{-1}\), respectively. More importantly, Al and Mg do not form dendrites after plating. Due to the stronger interaction with O atoms, the diffusion barrier of multivalent ions (Al, Mg, Ca) on O-terminated MXenes’ surface (>0.5 eV) is larger than that of the monovalent ions (La, Na, K, <0.3 eV). Therefore, the calculation multivalent ion battery may have high capacity, but their rate performance would not be as good as the monovalent ions. However, on bare MXenes’ surface, all the barrier decrease to <0.1 eV, except Al, but still not larger than 0.15 eV. Thus, a bare surface would be desirable for high energy and power density multivalent ion battery.

In contrast to the predicted high capacity, MXenes still do not exhibit a high Mg storage ability. CTAB-pillared Ti\(_3\)C\(_2\) MXene paper (figure 6(a)) delivered capacities of 100, 80, 67, 53, and 42 mAh g\(^{-1}\) at current densities of 0.05, 0.1, 0.2, 0.5, and 1 A g\(^{-1}\), respectively (figure 6(c)) \([59]\). The theoretical capacity should be 292 mAh g\(^{-1}\) if stochiometric ratio of Mg\(^{2+}\)/Ti\(_3\)C\(_2\)O is 1. It means probably the first-layer
adsorption of Mg was not realized, let alone the predicted one or two additional layers. But the claimed poor rate performance is in accordance with the present results, which only exhibits 100 mAh g\(^{-1}\) at 0.05 A g\(^{-1}\) (C/6), and quickly dropped to 42 mAh g\(^{-1}\) at 1 A g\(^{-1}\). It is supposed that the interlayer spacing plays an important role in the Mg storage performance of MXenes. Pristine Ti\(_3\)C\(_2\) paper almost cannot store Mg (<2 mAh g\(^{-1}\) at 0.05 A g\(^{-1}\)), but CTAB-pillared MXenes owned much improved capacity (100 mAh g\(^{-1}\) at 0.05 A g\(^{-1}\)). It was attributed to the expanded interlayer spacing from 1.32 nm (Ti\(_3\)C\(_2\)) to 1.52 nm (CTAB/Ti\(_3\)C\(_2\)) (figure 6(b)). When Ti\(_3\)C\(_2\) MXenes were assembled into a porous structure with high surface area and pre-intercalated with Mg ions, the Mg\(_{0.021}\)Ti\(_3\)C\(_2\) electrodes deliver a capacity of ~210 mA h g\(^{-1}\) at 0.5 C [60]. The high surface area provides easily-available adsorption sites for Mg, and pre-intercalated Mg ions expand the interlayer spacing. Interestingly, the capacity increased with cycling for MXene-based film electrode [61, 62] because the accessibility of electrolyte and Mg was improved due to the interlayer expansion. It also reveals the significance of space for Mg storage, which needs large space for predicted multilayer adsorption [46]. The mechanism of Mg\(^{2+}\) storage in MXenes was investigated in APC electrolyte [60]. Two distinct plateaus imply two different steps. The first plateau at ~2.0/2.4 V corresponds to a reversible intercalation of ions, noticeably, the ion is RMgCl (R = phenyl) rather than bare Mg\(^{2+}\). The second plateau at ~0.8/1.9 V was assigned to a redox reaction between Mg ions and Ti\(_3\)C\(_2\)Tx, which is an irreversible conversion-type reaction due to the large activation barrier to recharge the Mg-containing compounds like MgO.

Till now, limited Al ion batteries based on MXenes are reported [63]. Vahid Mohammadi and co-workers revealed a rechargeable intercalation of Al ion in V\(_2\)CT\(_x\) MXenes, using high-purity aluminum foil as anode and AlCl\(_3/\)EMIm]Cl ionic liquid as electrolyte [64]. The capacity of V\(_2\)CT\(_x\) could be improved by delaminating stacking multilayer (ML-)V\(_2\)CT\(_x\) to few-layer (FL-) sheets, and could be further enhanced by using TBAOH intercalation for interlayer expansion (figure 6(d)). And the TBAOH treated few-layers exhibited a quite large capacity of 300 mAh g\(^{-1}\) at a high current density of 100 mA g\(^{-1}\) (figure 6(e)). It is demonstrated the important roles of interlayer space and surface area for multivalent ion storage. However, there are still lots of questions to be answered, e.g. whether Al\(^{3+}\) intercalates with organic molecules or not, why there is a slow and continuous decline in capacity during cycling.

4. Conclusions and perspectives

MXenes are unique and excellent 2D materials for energy storage. The strategies to enhance energy and power density depend on the surface chemistry. Thanks to the 2D structure, heterostructures of MXenes are sophisticated design with microscale orderliness and function complementary to well incorporate with different materials to display an improved performance. 2D structures could form the low-tortuosity electrode with vertically aligned nanosheets, decreasing the ion diffusion resistance for high rate performance. MXenes are a handful of materials with reversible intercalation of various metal ions (Li\(^{+}\), Na\(^{+}\), K\(^{+}\), Mg\(^{2+}\), Al\(^{3+}\), etc.), emerging as promising cathode materials for multivalent ion batteries with high capacity and low cost. An expanded interlayer spacing is proved to be highly necessary to accommodate multilayer metal ion adsorption for high capacity. Surface groups on MXenes play vital roles for energy storage. O-terminated and bare MXene are favorable compared with F- and OH-terminated ones in terms of multilayer ion adsorption and ion diffusion barrier. Moreover, surface groups could control the in-situ growth of other active materials with monodispersed nanoparticles, preventing the aggregation in the charge–discharge process.

MXenes have achieved great success in energy storage. However, there are still many issues to be addressed to improve the performance. (1) The intercalation mechanism of multivalent ions into MXenes needs to be figured out in detail, e.g. whether the ions intercalated with solvated shells or not and how to work, what is the substantial role of the interlayer spacing, revealing mathematic relationship between interlayer spacing and diffusion behavior, and multilayer adsorption through experiments. (2) Lots of MXenes are reported with high capacity and rate performance, but practical application is still absent. Experiments are very desirable to verify their performance, and this requires the innovation of synthesis and etching methods. (3) The influence of surface groups was mainly focused on ion adsorption and diffusion. More groups with different functions, such as storing metal ions, with ion/electron conductivity, or pillared within interlayer, are worth deep investigation. (4) Doping and defects have been widely introduced into MXenes’ layers, however, the application are limited as catalysts for splitting water. The potential of doping and defects of MXenes in energy storage is unexplored. It is believed that, with the development of experiments and calculations in detail, new breakthroughs in power and energy density of MXene will be obtained in the near future.
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ORCID iD

Chengxiang Wang https://orcid.org/0000-0002-3907-5582

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