JPhys Energy

TOPICAL REVIEW • OPEN ACCESS

MXene for energy storage: present status and future perspectives

To cite this article: Pratteek Das and Zhong-Shuai Wu 2020 *J. Phys. Energy* **2** 032004

IOP Publishing J. Phys. Energy 2 (2020) 032004 https://doi.org/10.1088/2515-7655/ab9b1d

Journal of Physics: Energy

OPEN ACCESS

RECEIVED
16 March 2020

REVISED
28 April 2020

ACCEPTED FOR PUBLICATION
9 June 2020

PUBLISHED
3 July 2020

TOPICAL REVIEW

MXene for energy storage: present status and future perspectives

Pratteek Das[1,2] and **Zhong-Shuai Wu**[1]

[1] Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, People's Republic of China
[2] University of Chinese Academy of Sciences, 19 A Yuquan Rd, Shijingshan District, Beijing, People's Republic of China

E-mail: wuzs@dicp.ac.cn

Keywords: MXene, battery, supercapacitor

Abstract

MXene is rising as a versatile two-dimensional material (2DM) for electrochemical energy storage devices. MXene has boosted the performance of supercapacitors thanks to its pseudocapacitive charge storage mechanism with electric double layer behavior. Further, MXene has helped batteries achieve high capacity while endowing fast charge-discharge by virtue of its suitable interlayer spacing and unique chemistry. Such achievements are a result of MXene's intrinsic properties like high electrical conductivity, defined layered structure and ability to sustain customizations, tailoring the electrodes towards a specific target. Not only that, MXene has showcased its merits by enabling supercapacitors and batteries to surpass the convention and venture into the territory of micro-supercapacitors (MSCs), hybrid capacitors and batteries beyond Li-ion. Herein, we present a topical review discussing the present status of MXene-based energy storage devices and corresponding challenges. By rational analysis, we also provide some key avenues for further research that may help overcome these shortcomings and enable this family of MXene materials attain its full potential.

1. Introduction

MXene is an emerging new material that is the outcome of a decade-long research on two-dimensional materials (2DMs) originating from graphene and extending to 2D polymers, metal oxides, transition metal dichalcogenides, and so on. In general, MXene is a family of 2D transition metal carbides/nitrides with randomly distributed functional groups on the surface, bearing the formula $M_{n+1}X_nT_x$, where M is transition metal, X is carbon and/or nitrogen, and T is a functional group like fluorine, hydroxyl or oxygen [1].

However, unlike the other 2DM counterparts, MXene has managed to earn the title of 'next wonder-material' in a very short span of time since its inception in 2011 [2–4]. It exhibits high electrical conductivity (2×10^5 S m^{-1}) at par with multi-layered graphene [5], reasonably large specific surface area [6], rich surface chemistry owing to its functionalization ability [7, 8], easy dispersion in a number of solvents including water [9], and most importantly astounding electrochemical properties conducive for energy storage applications. These properties arise intrinsically within MXene for a number of reasons. These include its 2D structure that allows fast ion transportation within 2D/3D channels [10], redox reactions that add a pseudocapacitive component to the electrical double-layer mode of charge storage [11, 12], and balanced mechanical flexibility at nanosheet level accommodating large ions for lithium ion batteries and beyond [13].

Such versatile attributes render MXene as a potential leading active material for batteries and supercapacitors. With the body of research on newer systems rapidly expanding, MXene is finding more applications for enhancing their performance. For example, conductive polymers (e.g. polyaniline, polypyrrole) have a number of properties that make them a suitable electrode material, but mostly in acidic medium, where they are more stable [14]. To fabricate asymmetric supercapacitors, MXene has been used as a negative electrode to achieve large potential window (1.45 V) in acidic electrolyte, thus increasing the energy density [15]. This is significantly higher than carbon-based materials, since they have low capacitance

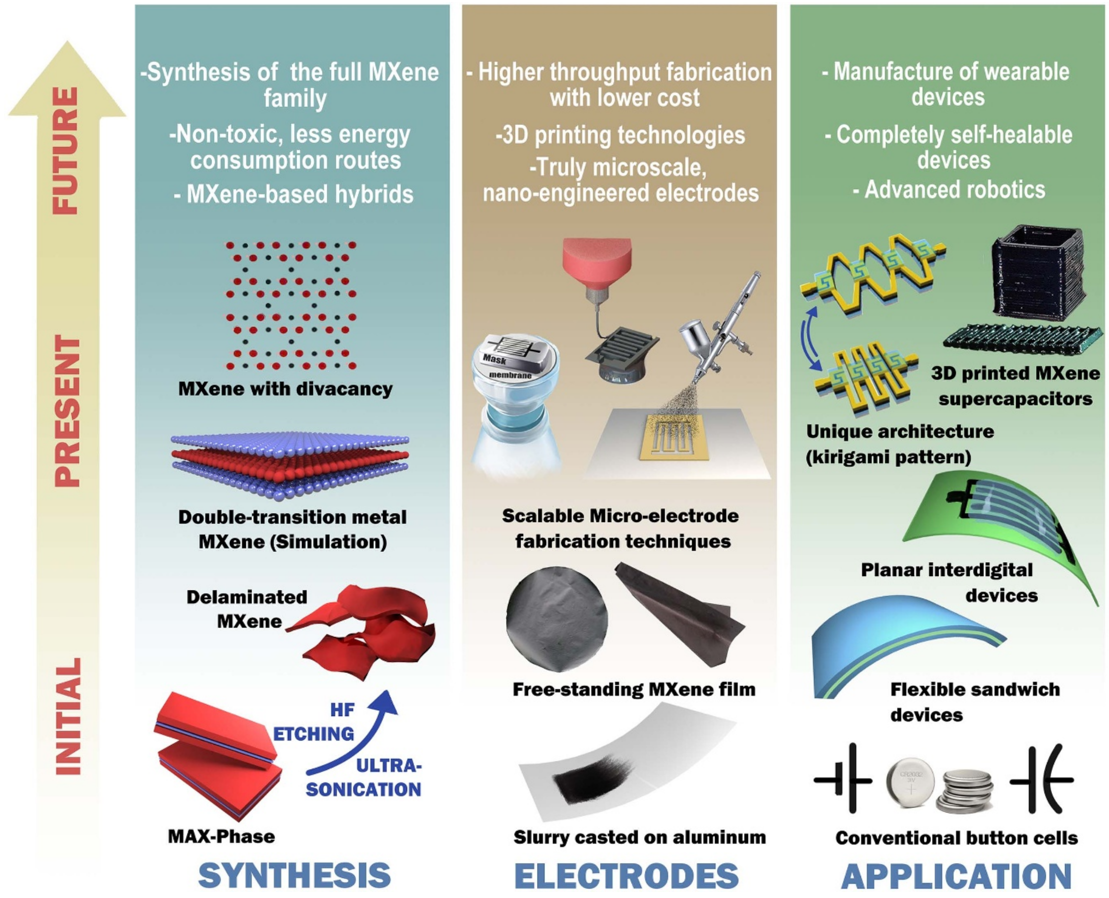

Figure 1. (Left) Evolution of synthesis goals for MXene, starting from the HF etching of MAX phase to the simulation of double-transition metal MXene [17] and the recent preparation of MXene with ordered divacancy [25]. (Copyright 2017, Nature Springer). (Middle) Development of electrode fabrication methods using conventional slurry-casting on aluminium, led way to free-standing MXene films prepared by vacuum filtration [26]. Copyright 2014, National Academy of Sciences. (Right) MXene-based batteries and supercapacitors have gone beyond traditional button cells to more flexible alternatives. Further they have been applied for unique architectures like kirigami patterns[22] (Copyright 2019, Wiley-VCH Verlag GmbH & Co. KgaA) and 3D printed devices[23] (Copyright 2020, American Chemical Society).

and narrower potential window (normally <1.0 V). Similarly, where the performance of carbon-related materials for Na/K ion or Li–S systems is saturating, MXene is picking up the mantle for pushing these systems to store greater quantity of energy by using hybridization [16].

The ideas for synthesis of MXene have gone beyond the single transition metal-based MXene towards the search for double transition metal-based MXenes [17]. Alternatives for HF-based selective etching are being sought after to make the whole process non-toxic figure 1 (left). For the preparation of electrodes, traditional techniques are being replaced by printing/stamping techniques for scaling up the devices for homogenized mass production [18–21] figure 1 (middle). With more and more restrictions being lifted off from the material and electrode fabrication, scientists are realizing challenging architectures for batteries and supercapacitors to broaden the scope of MXene's applications [22–24] figure 1 (right).

However, currently MXene is far from being the solution to every energy storage-related problem. In fact, MXene itself has several shortcomings that researchers are working hard to overcome. This topical review focusses on the recent developments in MXene-related materials with multiple functionalities pertaining to energy storage in the form of advanced supercapacitors and new-generation batteries. We try to concisely explain MXene's role in pushing energy storage devices towards higher performance and inspiring new architectures to tackle the related drawbacks rationally.

2. MXene-based supercapacitors

2.1. MXene as an active material

Supercapacitors come in various shapes and sizes. Classifying them properly is a tedious task which has been done masterfully before [27]. However, it is interesting to note that MXene has been used as active material to enhance the performance of almost all kinds of supercapacitors. From conventional rigid sandwich

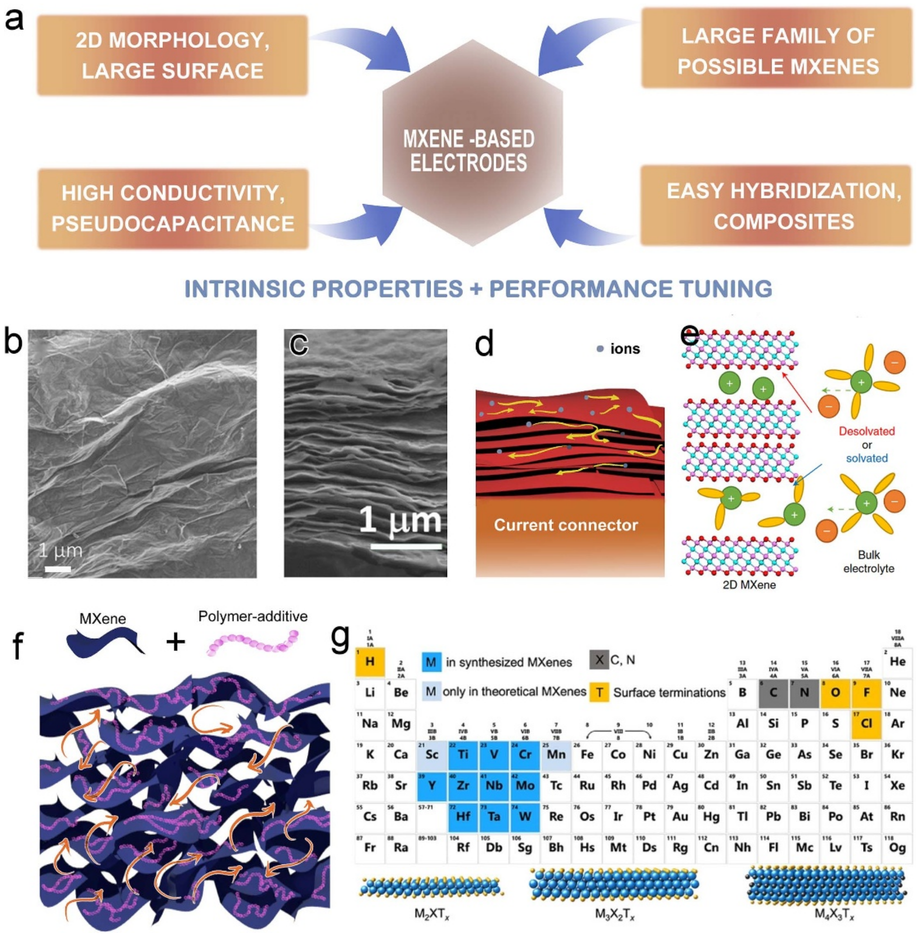

Figure 2. (a) The properties of MXene that makes it suitable as an active material for supercapacitive electrodes. (b) SEM image of a normal MXene film showing the 2D morphology and wrinkled surface [18]. Copyright 2018, Wiley-VCH Verlag GmbH & Co. KgaA. (c) Cross-section SEM image of MXene film showing the layered stacking of multiple layers [29]. Copyright 2020, Wiley-VCH Verlag GmbH & Co. KgaA. (d) Schematic of typical in-plane ion transport channels in a MXene film. (e) Pseudocapacitive intercalation mechanism of MXene-based supercapacitor electrodes responsible for the typically high capacitance of bare MXene [45]. Copyright 2019, Nature Springer. (f) Schematic showing the synergistic effect of MXene with certain additives (for example PEDOT:PSS [35]) that may help maintain interconnected porous structures and high conductivity both for ions and electrons (arrows showing the unhindered pathways for ion transport). (g) Periodic table showing the family of MXenes (and MAX phases) that have been theoretically predicted and/or experimentally synthesized. Below are the three likely structures for MXenes [46]. Copyright 2019, American Chemical Society.

supercapacitors for demonstrating high-volumetric capacitance and studying mechanism[28] to ultra-flexible interdigital MSCs [29] for proving the future of MXene in powering microscale electronics with various form-factors, it has covered a wide spectrum. Active materials in supercapacitors are chosen based on the targeted application because different intrinsic properties can optimize a particular parameter. For instance, if a material has large active surface area that is accessible to electrolyte ions, it will contribute greatly to the electrical double-layer capacitance, typically, carbon-based materials like graphene [30]. However, this is not enough to meet the demands of future micro-electronics that require high energy output from small footprint. Therefore, transition metal dichalcogenides and transition metal oxides are introduced to enhance energy density of supercapacitors [31]. But they lack high electrical conductivity of carbon, making it necessary to use carbon-based binder or current collectors to improve their rate performance. In this regard, MXene has emerged as a great solution to this conundrum. Being a 2DM, MXene has high surface area providing electrical double-layer capacitance (figures 2(b)–(d)). Simultaneously, it gives a huge boost to pseudocapacitance through an intercalation mechanism accommodating a wide variety of cations (figure 2(e)) [28]. Not only that, MXene reflects a redox-active surface with acidic electrolyte that has helped it achieve landmark volumetric capacitance of 900 ~ 1500 F cm^{-3} [32, 33]. It is worth noting that the materials that usually rely on redox reactions or intercalation mechanisms have sluggish rate performance making them unsuitable for high rate applications like AC-line filtering [34]. But it has been recently demonstrated that a simple mixture of MXene with conducting polymer poly(3,4-ethylenedioxythiophene) poly-styrene-sulfonate (PEDOT:PSS) leads to retention of mesopores, ensuring fast ion transportation (figure 2(f)). Further, it was speculated that PEDOT's doping/redoping process facilitated a surface redox mechanism that allowed the hybrid to not only show high capacitance at low scan rates but also retain high capacitance (10.8%) at very high scan rates, e.g. at 1000 V s^{-1} [35]. Therefore, it is evident that MXene can serve as a multi-functional active material for supercapacitors.

The discussion above draws attention towards the significance of doping or surface modification to boost the performance of electrochemical energy storage devices. By definition, doping is the process of adding impurities to a material to achieve desired response, e.g. the enhancement of electrochemical performance in our case. The achievements of graphene doping reported so far has been carried over to MXene-based supercapacitors [12, 36, 37]. Doping of MXene can achieve either surface modification or pillaring. The immediate effect visible from doping is the change in bandgap [38]. This is associated with a transition towards more metallic character of MXene nanosheets which is always welcomed. It has been demonstrated both theoretically and experimentally that replacing the hydroxyl/fluoride functional groups with sulphur can promote the adsorption of multiple layer of counter-ions which is conducive for high pseudocapacitive charge storage [39]. For 2DMs, increasing the interlayer spacing directly translates to the enhancement of intercalation pseudocapacitance. Pillar-doping modifies the electrochemical kinetics of MXene and accommodates large quantity of counter-ions [40, 41]. Additionally, the synergy between different atoms (heteroatom doping) can be exploited to simultaneously improve electronic property of electrode while enhancing the interaction with electrolyte from respective dopants [42, 43]. However, one should be cautious while doping, because even a small excess in dopants can cause steep decline in capacitance [44].

Last but not the least, there are many more promising MXenes suitable for supercapacitor applications that have been theoretically predicted but yet to be realized experimentally (figure 2(g)). It is urgent for us to probe deeper into the MXene family for squeezing out every possible enhancement related to supercapacitor electrodes.

2.2. Enhancing the voltage window

A key problem of MXene for supercapacitors is the low upper limit on the voltage window (0.6 V) in conventional salt/acidic solutions [47]. The properties and trade-offs related to different electrolytes/solvents is summarized in figure 3(a). It is well known that extending the potential window can greatly increase the energy density. One of the most viable method is to use electrolytes that do not decompose through reaction with the electrodes. In this sector, aqueous electrolytes have lagged behind due to their small window of only 1.23 V. Organic solvent-based electrolytes have been proposed to increase the voltage window (~2.4 V) [45], Moreover, different organic solvents yield varying degree of intercalation into the MXene interlayers leading to a huge difference in total charge stored (figure 3(b)) [45]. However, they may be flammable and toxic raising serious safety concerns. Therefore, it is fortuitous that the surge in research on novel electrolytes, such as water-in-salt or hydrate melts have benefited MXene-based supercapacitors. Such systems have shown an increase in potential window from 0.6 V to nearly 1.2 V (figure 3(c)), consequently more than doubling the energy density from 20 to 45 mAh g^{-1} [47]. The MXene is presumably protected by the formation of solid-electrolyte interphase, but, this comes at the cost of rate performance resulting from the lack of direct coordination between water molecules that are primarily responsible for fast ion transport in conventional aqueous electrolytes. In-depth experimental and theoretical studies have pointed towards a contact-ion-pair dissociation mechanism (both at bulk and surface) as the primary reason for such sluggish rate capability of hydrate melt electrolytes [48]. Another strategy to achieve broad potential window (up to ~3 V) has been the use of ionic liquid or ionogel electrolytes [49, 50], however, the current research on them is still at its infancy and needs further progress to output greater current densities. In addition to electrolyte optimization, asymmetric supercapacitors may be designed with MXene as negative electrode and other matching materials like α-MnO_2 as positive electrode to compensate the trade-off between voltage window and capacitance (figure 3(d)) [51]. Such supercapacitors show large voltage window of 2 V and high areal capacitance of 295 mF cm^{-2} which together manifest as high energy density. The future supercapacitors may benefit from such synergy produced by combining two completely different approaches to achieve the same goal.

2.3. MXene for micro-supercapacitors

MSCs are one of the most important micro-electrochemical energy storage devices, where the effect of MXene as microelectrodes is starkly visible. By offering high capacitance, outstanding conductivity and flexibility, MXene-based MSCs (M-MSCs) have aided the further reduction in volumetric and areal footprint of supercapacitors [23, 51, 53–56]. So far, a majority of the studies on MXene-based MSCs (M-MSCs) make use of the planar interdigital architecture. Several intuitive advantages merit this structure, including quick ion transport between edges of the microelectrode fingers, reduction in overall device thickness, good matching of 2D structure with planar geometry, and easy integration with on-chip electronics (figures 4(a)–(c)) [57]. Usually, the synthesis of MXene follows a wet chemical etching of MAX phase in concentrated hydrofluoric acid which requires solution processing [18, 58, 59]. Therefore, the predominant routes for

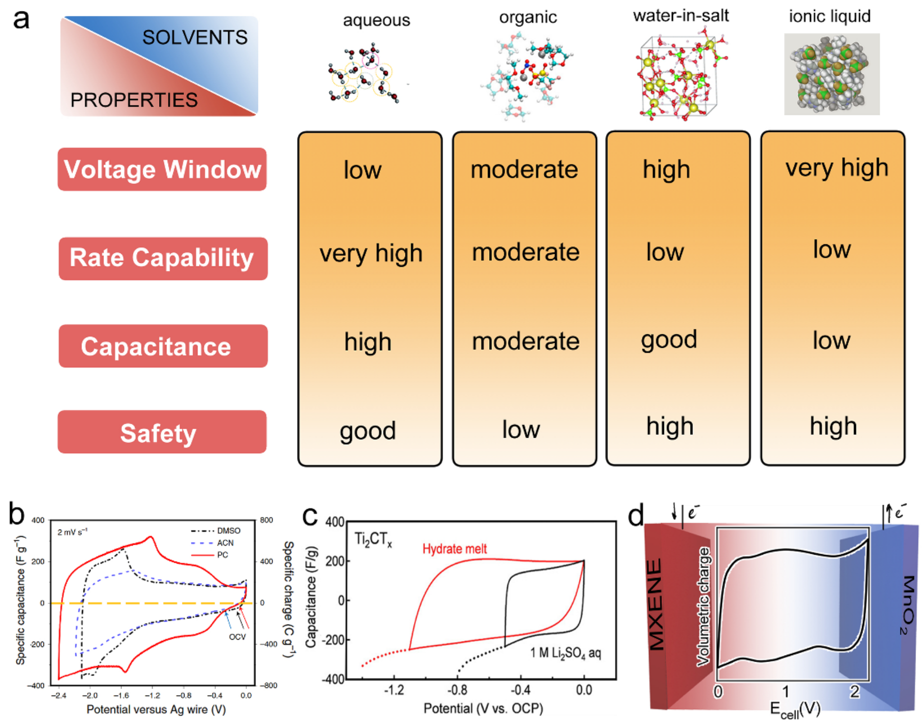

Figure 3. (a) Effects of different types of solvents on performance and safety of MXene supercapacitors. (b) Cyclic voltammetry (CV) curves showing the difference caused by using different organic solvents (dimethyl sulfoxide, acetonitrile and propylene carbonate) in terms of chemical reactions and ion intercalation [45]. Copyright 2019, Nature Springer. (c) CV curves showing the effect of increasing concentration of electrolyte in water leading to an increase in voltage window but decrease in rate capability (evident from shape) [47]. Copyright 2019, American Chemical Society. (d) Schematic showing MXene//α-MnO_2 asymmetric supercapacitor with enhanced voltage window (CV shown was reproduced from ref. [52]). Copyright 2019, Elsevier.

fabricating M-MSCs have been vacuum filtration[49], spray-printing [60, 61], screen-printing [20], and stamping [18]. The substrate ranges from different kinds of rigid silicon wafer to flexible filter papers and polymer films. This is the biggest advantage of M-MSCs. Added to the excellent areal capacitance obtainable from M-MSCs [18, 62, 63], they offer outstanding flexibility which allows their adaptation to various shapes and opens up broad prospects of applications. Polymer-based gel electrolytes are arguably the most suitable for such MSCs because they add a key factor of safety. Further, such quasi-solid-state electrolytes can push the flexibility to its limits as demonstrated by our group from their extremely deformable planar M-MSCs by exploiting encapsulation of planar MXene-based microelectrodes inside hydrogel electrolyte [29]. However, a major drawback in planar M-MSCs is the low volumetric energy density. This has been tackled to some extent by designing asymmetric M-MSCs with complementary electrodes like MnO_2 that extend the voltage window [51], selecting different electrolytes to suppress high voltage decomposition/side reactions [26], or by applying unique methods to create flexible 3D microelectrode arrays [23]. Simple thicker microelectrodes may result in the reduction of volumetric capacitance and sluggish rate capability, whereas thick porous microelectrodes while boosting areal capacitance may sacrifice its volumetric counterpart, necessitating a trade-off in the design and areal/volumetric performance of microelectrodes. However, the ease of fabricating M-MSCs with different form factors using high throughput techniques such as screen-printing [64] and demonstration of one-step integration with microelectronics (e.g. sensors) [20] certainly raise hopes for the bright future of planar M-MSCs.

Apart from small-scale applications, MXenes have witnessed a greatly boosted performance in terms of specific areal capacitance aided by 3D printing technology. Recently, a rigid 3D printed, freestanding M-MSC has been reported with an astounding areal capacitance of 2 F cm^{-2} at current density of 1.7 mA cm^{-2} (figures 4(d) and (e)) [24]. Main attraction is the property scaling with the thickness of electrodes and the variety of shapes that can be easily realized by increasing the number of layers. However, such increased capacitance comes at the cost of flexibility. MXene itself has limited stretchability, which could be greatly enhanced by compositing with other 2DMs. Very recently, Gogotsi's group demonstrated an additive-free MXene-reduced graphene oxide composite with high resistance to damage under strains greater than 250% in uniaxial or biaxial directions [66]. A competitive capacitance of 19 mF cm^{-2} could be well retained at nearly 100% even after 1000 cycles. Such stretchability ensures damage resistance and is a crucial parameter for wearable MSCs. But the ultimate test for them is self-healing because it takes restoration from damage to

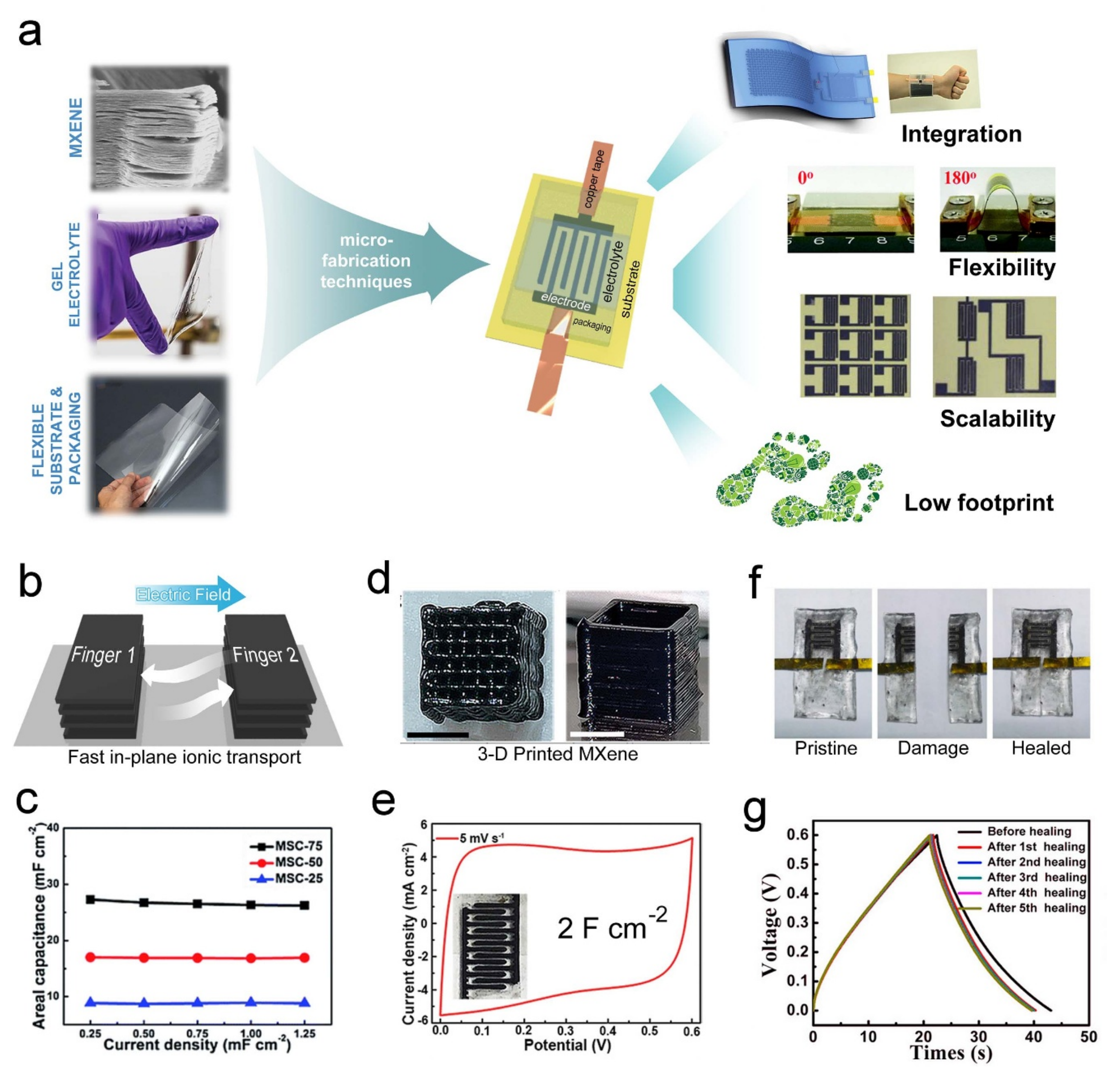

Figure 4. (a) Schematic showing the ingredients required for fabricating M-MSCs and their subsequent advantages. (b) Schematic showing the fast ionic transport between two adjacent fingers in planar M-MSCs occurring in the lateral plane. (c) The plot of areal capacitance *vs.* current density highlighting the incredible rate capability available from such architecture of M-MSCs (MSC-25 to 75 represent different thickness of electrodes) [63]. Copyright 2017, Royal Society of Chemistry. (d) 3D printed structures made using MXene ink. (e) Thick M-MSCs made by 3D printing can offer capacitance as high as 2 F cm^{-2} [24]. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KgaA. (f) Photographs demonstrating self-healable MXene-graphene MSC at different stage of damage and recovery, and (g) corresponding galvanostatic charge-discharge (GCD) profiles obtained at different healing cycles showing excellent healing efficiency [65]. Copyright 2018, American Chemical Society.

the next level. Although currently available self-healable supercapacitors are far from being applicable in wearable systems, the demonstrations of working prototypes are impressive. MXene has also entered as a competitive active material that is compatible with different self-healing approaches. A common self-healing approach is coating a quasi-solid state supercapacitor with a self-healable polymer like carboxylated-polyurethane [65]. In this case, MXene-based composite itself cannot recover from breakage, but if aligned properly may restore electrical connection (with small conductivity loss). This method has a decent recovering efficiency evident from the retention of 81% capacitance (figures 4(d), (f)–(g)), but the internal resistance increases by nearly 50 Ω over five healing cycles. Consequently, it is even more desirable to create MXene-based electrodes that are intrinsically self-healable [67]. However, no such work has been reported so far. Nevertheless, recent experiments on integrating MXene into self-healable viscoelastic material [68] and demonstration of their dielectric-based capacitive behaviour [69] would be a stepping-stone for realizing fully healable MXene-based supercapacitors.

3. MXene-based batteries

3.1. MXene for lithium-based batteries

Rechargeable lithium ion batteries (LIBs) brought about the much needed but rather unexpected rise of electrical vehicles and portable electronics by reducing the dependence on a fixed power source, thanks to the

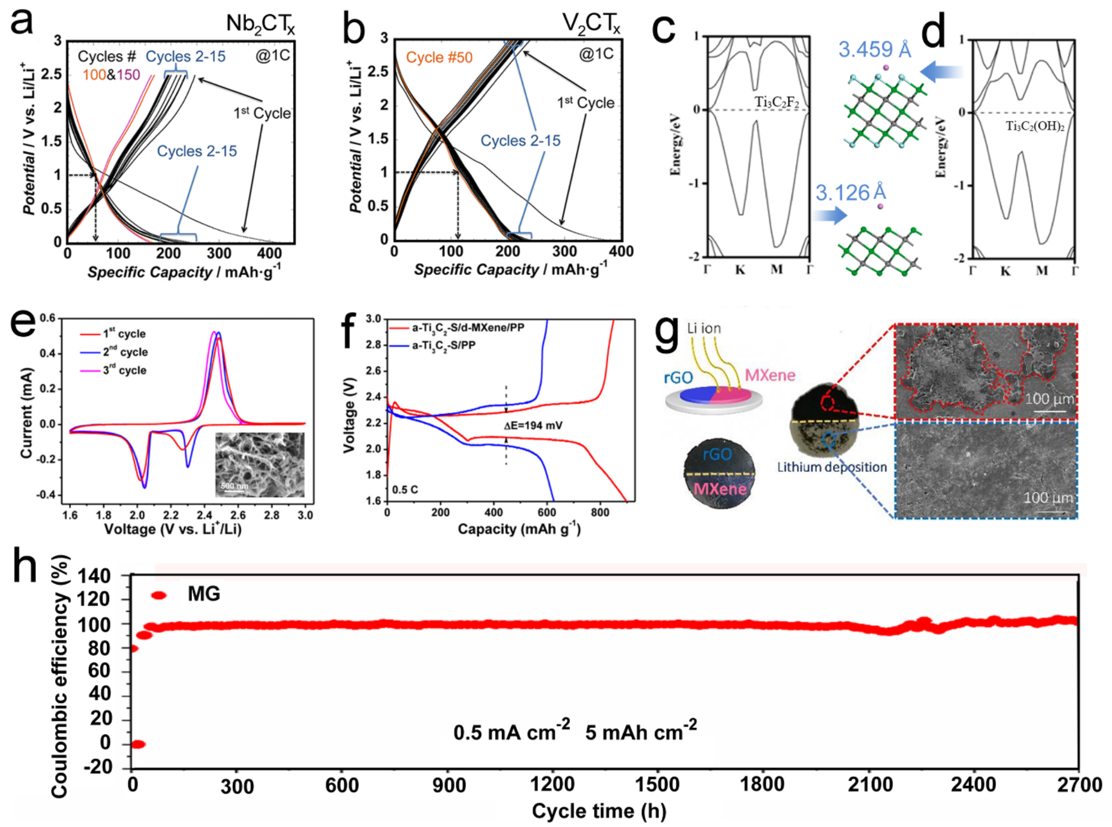

Figure 5. (a), (b) Voltage profile of Nb$_2$ CT$_x$ and V$_2$CT$_x$ *vs.* Li/Li$^+$ in different voltage ranges [1]. (c), (d) Near-Fermi level band structure for Ti$_3$C$_2$F$_2$ and Ti$_3$C$_2$(OH)$_2$ respectively and the corresponding Li to C distance in case of optimized lithiation illustrating the effect of functional group on lithium uptake behaviour [76]. Copyright 2012, American Chemical Society. (e) CV curves and (f) GCD profiles of Li-S batteries with electrodes composed of sulphur hosted in Ti$_3$C$_2$ nanoribbons. Inset in (e) shows the SEM image of Ti$_3$C$_2$ nanoribbon and sulphur hybrid [78]. Copyright 2018, American Chemical Society. (g) Photograph and SEM image of lithium deposition on graphene and MXene showing advantage of uniform distribution of lithium on MXene film [79]. (h) Coulombic efficiency of MXene/graphene-Li anode obtained at a current density of 0.5 mA cm^{-2} over 2700 h [79]. Copyright 2019, American Chemical Society.

large energy density [70, 71]. In particular, the research on LIBs is focussed on catching up with the miniaturization of electronics by increasing energy density and reducing footprint while charging faster [72–74]. Unsurprisingly, MXene has joined the fray as a strong competitor because it not only enhances LIBs but also promises viable expansion into batteries beyond Li-ion.

MXene was first tested as a LIB anode material by Naguib *et al* in 2011 and showed promising results due to its high specific surface area, weak interlayer forces, open structure and surface functional groups [75]. Since MXene consists of M (early transition metals), X (C and/or N) and T (functional groups of O, OH and F), a large number of permutations are possible which can be used for tuning the performance. For instance, the specific capacity of different MXenes follows the order Ti$_2$C < Nb$_2$C < V$_2$C while both Nb$_2$C and V$_2$C show high rate capability [1]. Moreover, the voltage profiles are significantly different among different MXenes, suggesting the suitability of different MXenes for either anode or cathode (figures 5(a) and (b)). Furthermore, the functional groups tend to possess fundamentally different band structure, for example, bare MXene is a magnetic metal while functionalized MXene is semiconductor. Also, they affect the Li uptake and transport [76]. Non-native functional groups like chlorides can give a steric advantage to MXenes by increasing the interlayer spacing and mitigate the detrimental effects of the native OH and F functional groups [77]. In fact, even stoichiometric ratios of 'M' belonging to the same species, prepared by varying fabrication process, can affect the capacity of LIBs indirectly due to the varying degree of surface properties. Typically, Ti$_2$CT$_x$ with higher surface energy than Ti$_3$C$_2$T$_x$ tends to have reduced *c*-lattice parameter, thus hindering the intercalation of Li ions [36].

To overcome the limit of theoretical capacity of bare MXene (Ti$_3$C$_2$, nearly 320 mAh g^{-1}) as anodes for LIBs [80], there is yet another way of applying MXene-based nanostructured electrodes for lithium–sulfur (Li–S) batteries which are predicted to reach up to 1675 mAh g^{-1} and large energy density of 2600 Wh kg^{-1} due to the multi-electron chemistry between Li and S [81]. But the well-known polysulfide shuttling effect results in fast capacity decay, and serious efforts have been dedicated to mitigate this [82]. Both theoretical and experimental evidences suggest the effectiveness of polysulfide-anchoring materials in alleviating this issue [83–85], and MXenes are coming to the forefront in this research. Recently, Dong *et. al.* reported all-MXene-based flexible and integrated sulfur cathode, enabled by three dimensional alkalized Ti_3C_2 MXene nanoribbon frameworks as S/polysulfides host and 2D delaminated Ti_3C_2 MXene nanosheets as interlayer, for high-energy and long-cycle Li–S batteries [78]. 3D MXene nanoribbon framework having conductive and interconnected porous structure greatly advanced electrolyte/electron diffusion to the interior of the electrodes, and 2D MXene interlayer remarkably prevented the shuttle effect of lithium polysulfides via both chemical absorption and physical blocking [86]. Most impressively, a capacity of 1062 mAh g^{-1} was achieved at 0.2 C (figures 5(e) and (f)). Furthermore, due to the strong chemisorption of sulphide on the titanium sites, the framework acted as a safety net. This greatly hindered the shuttling behaviour, resulting in long cycle life (200 cycles) at nearly 100% coulombic efficiency, with assistance of MXene nanosheet-interlayer coated on polypropylene separator. Further, another report has suggested that the thickness of the MXene layer on separator must be regulated to balance the trade-off between shuttling suppression and lithium ion transport across the separator [87]. As far as surface terminations are concerned, it is worth noting that different functional groups, e.g. O and S based terminated groups, have been shown to improve the sulphur (and polysulphide) anchoring strength compared to bare MXene [88]. Also, nitrogen-doping has been proposed to assist MXene in increasing physical anchoring and efficient catalytic conversion of polysulphide and promoting fast sulphur reaction kinetics [89, 90]. These results further consolidate the position of MXene with 60+ members in its family and corresponding heterostructures/composites as promising materials for next-generation Li–S batteries [91].

It should be noted that rechargeable LIBs with low-capacity graphite anodes came along as a substitute for batteries with lithium metal anodes despite them having the highest theoretical capacity (3860 mAh g^{-1}). The reason for such shift was the largely unresolved safety concerns arising from the infinite volume expansion of anode and subsequent dendrite formation that punctured the separator and short-circuited the cell, causing explosive fires. However, eyeing the huge available capacity, researchers have continued to explore these avenues in the form of mechanism studies, additives and hosts for making Li metal-based batteries safer [92–94]. Quite recently, MXene has also contributed to this area by acting as an efficient 3D lithiophilic host [79]. The MXene-based 3D framework allows uniform distribution of lithium (figure 5(h)) that remarkably suppresses the dendrite growth while retaining a large current density even at high Li-loading of 92%. As a result, 2700 h of operation with 99% coulombic efficiency at 0.5 mAh cm^{-2} was achieved (figure 5(i)). The trick is to homogenize the growth of dendrites by using 3D framework for the formation of stable solid-electrolyte interphase[95, 96] or homogenous nucleation of Li-dendrites on the surface of host by using techniques like nanoparticle doping [97]. MXene is particularly beneficial as a substrate for this nucleation strategy because it offers large surface area, high conductivity and lithiophilic properties. This guarantees directional growth of lithium dendrites in bowl-like shapes and avoids infinite volume expansion while retaining higher volumetric capacity of 40 mAh cm^{-2} for 1200 h, compared to the porous 3D counterparts [98].

3.2. MXene promoting beyond-lithium batteries

Lithium-based batteries are undoubtedly the most researched and reviewed ones in scientific literatures. But the impending realization that lithium resources are not abundant in Earth's crust and will soon suffer a similar fate as fossil fuels with over-consumption, leads us to look beyond lithium. Fortunately, the works on other metal ion batteries, including Na, K, Al, Mg, Zn and so on, are picking up pace by borrowing heavily from the research put into LIBs. Although their theoretical capacity is lower than lithium [99, 100], they can relieve the pressure on lithium resources by acting as alternate energy storage systems.

Although these ions have large ionic radii compared to lithium, they still exhibit high rate capability, which is likely due to high electronic and ionic conductivity in these MXene with extended interlayer spacing (figure 6(c)) [99, 101]. Mechanically, MXene can accommodate the stress from volume expansion of the added nanoparticles and prevents their pulverization during (de-)sodiation while the nanoparticles reduce the surface energy and prevent restacking of MXene. Electronically, the nanoparticles may assist to better overlap the conduction and valence band, making it easier for MXene to donate electrons (figure 6(b)) [102]. The electronic conductivity is intrinsic to MXene but the ionic counterpart is more interesting where a hopping of Na and K ions at the top Ti and C sites of the MXene is evident. This mechanism that allows reduced diffusion barrier changes for multivalent ions like Al^{3+} which causes a horizontal sliding of MXene's monolayer. This diffusion barrier can be further reduced, at least for Na^+ ion by hybridizing MXene with other nanomaterials like black phosphorus or transition metal oxides to further enhance specific capacity (>400 mAh g^{-1}) and stability [102, 103].

The reason for MXene's excellent ability to handle large ions compared to graphene has been systematically studied using simulations. MXene with two layers of Li, Na, Mg, K and Ca adsorbed ions

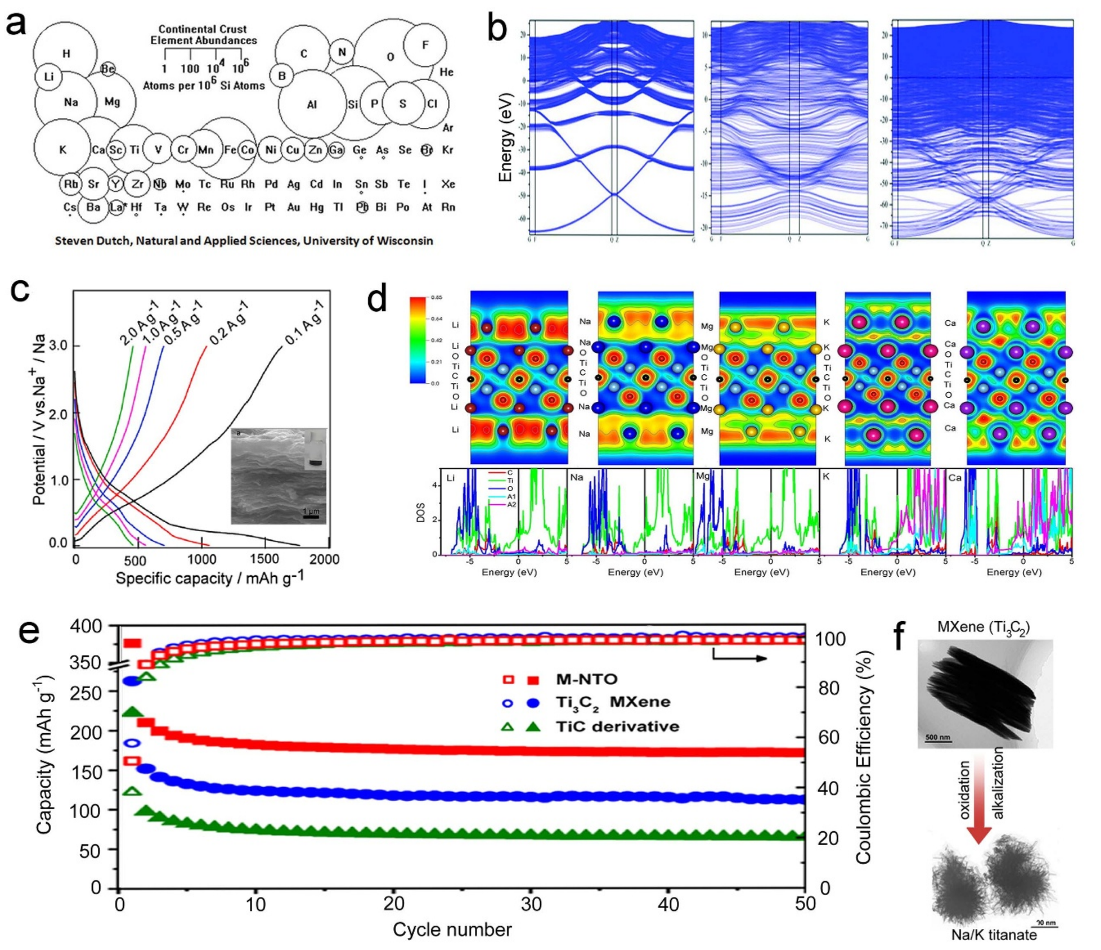

Figure 6. (a) Relative abundance of different metals in Earth's crust [114]. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KgaA. (b) Electronic band structure of MXene (Ti_3C_2), phosphorene and their composite from left to right [102]. Copyright 2019, Royal Society of Chemistry. (c) GCD profiles of layered 2D phosphorene-MXene heterostructure electrodes for Na-ion batteries obtained at different current densities. Inset is the cross-sectional SEM image of the active material elucidating the molecular nanosheet level heterostructure [101]. Copyright 2019, Elsevier. (d) Electron localization functions for Li, Na, Mg, K, and Ca and corresponding projected density of states of MXene with two metal layers adsorbed [99]. Copyright 2014, American Chemical Society. (e) Cycling stability and coulombic efficiency of MXene derived sodium titanate (NTO) for sodium ion battery [16]. (f) Schematic showing conversion of MXene to NTO via oxidation and alkalization [16]. Copyright 2017, American Chemical Society.

exhibit similar electronic structures and adsorption energies showing similar effects in reducing repulsion between adsorbed atoms by a screening effect (figure 6(d)). However, similar to lithium's chemistry in MXene-based LIBs, hydroxyl and fluoride terminations are detrimental to Na and K ion batteries [99]. Notably, it has been predicted from first principle calculations that replacing –OH and –F groups with P and Si would boost Li capacity to values in excess of 1200 and 1700 mAh g^{-1} respectively. Similarly, this trend is also expected for Na and K ion batteries [104], due to the possible enhancement of the metallicity of MXene, reduced ion diffusion barrier and multilayer alkali ion adsorption enabled by surface modification [105].

Interestingly, MXene can also be converted into sodium/potassium titanate by step-wise oxidation and alkalization which are known to boost very high capacity for Na^+ and K^+ ion storage due to the desirable interlayer spacing (figures 6(e) and (f)) [16]. To maximize the number of electroactive sites, 3D porous structures could be constructed by compositing MXene with N-rich carbon nanosheets. It is noted that the N-doping effectively increases electrical conductivity and accessible surface area for alkali ion adsorption [106]. This could also be achieved by 'pillar-doping' with large ions, similar in principle to MXene-based supercapacitors [107].

While Na^+ and K^+ ion batteries readily flourished, multivalent ion batteries (e.g. Al^{3+}, Mg^{2+}, Ca^{2+}, Zn^{2+}) have, in general, been slower to be adopted. Although a state-of-the art V_2CT_x MXene based rechargeable Al battery has demonstrated a high specific capacity beyond 300 mAh g^{-1} at high current density of 100 mA g^{-1}, an explanation for the continuous capacity decay upon cycling is yet to be found

[108]. Surface modification of $Ti_3C_2T_x$ MXene with other nanoparticles like sulphur and TiO_2 has shown to improve stability with capacity retention increased from 26.5% to 72.3% after 120 cycles. The discharge capacity was also enhanced from only 65 mAh g^{-1} to 151.3 mAh g^{-1} (measured after 120 cycles) [109]. Previous reports of MXene-based multivalent ion batteries have shown a heavy reliance on intercalation of ions as the primary route for charge storage and rapid capacity decay after few thousand cycles has plagued all of them [110]. But a recent report on V_2CT_x-based zinc ion battery exhibited surprising capacity increase to 508 mAh g^{-1} over 18 000 cycles [111]. Closer inspection revealed that the intercalation mechanism had been overtaken by different chemical reactions arising from gradual phase change of V_2CT_x to V_2O_5. Such works suggest that unconventional routes are required to solve these conventional problems.

Multivalent ionic species do have several attractive features like higher charge to radii ratio, greater abundance than lithium and safety; but several shortcomings still have not been overcome. Despite their being plenty of theoretical research on the intercalation of multivalent ions into MXene interlayers giving rise to high capacity [112, 113], the number of experimental evidences corroborating the predictions are few. The problems range from lack of suitable electrolyte to inefficient plating/stripping of the anode or excessive strength of bonding between the MXenes and intercalating ions.

4. Future perspectives and challenges

In summary, we have presented some key development and issues related to MXene-based materials for supercapacitors and batteries. The number of studies on MXene is growing exponentially, and we are optimistic that most of the issues may be addressed by pushing the research on MXene in the right direction. Therefore, in the following paragraphs we provide a few possible research directions that deserve continuous attention and present us with great opportunities [115].

For supercapacitors, the specific surface area of MXene is lower than graphene, which if brought to the same level could in principle boost its specific capacitance and energy density. This can be achieved by adopting new strategies like concentrated acid + base treatment [120] for inducing pores into the electrodes to overcome drawbacks of MXene's rigid nanosheets (figure 7(a)). This could further allow more space for hosting a range of pseudocapacitive nanoparticles and accommodating the suitable ions of high-voltage electrolytes to further increase the energy density. The recent surge in different metal ion-based capacitors, such as Li, Na, K, Zn ion capacitors, must be pushed forward to achieve higher voltage[121] or rate capability [115]. *In-situ* characterizations have been performed before with Ti_3C_2 MXene electrodes in H_2SO_4 electrolyte (figure 7(b)) [62], and it stands to reason that other members of the MXene family with different electrolytes like ionic liquids and water-in-salt may benefit from such experiments.

In an era where electronics devices are occupying smaller spaces, compact energy storage devices like supercapacitors are needed to catch up with this trend. MXene has already made rapid progress in enhancing the volumetric capacitance compared to its predecessor graphene. But it can be further improved by optimizing both physical and chemical aspects. Physically, more compact electrodes are desirable that strike a balance between mass density and porosity. Currently, a wave of emerging printing technologies like continuous centrifugal coating [122], can be extended to produce the fabrication of highly compact MXene-based microelectrodes. Further, pore-engineering in MXene electrodes should be emphasized in future researches. But given the brittle nature of MXene nanosheets this is difficult to achieve by physical techniques. This is where chemical modification comes into play. Just modifying the surface terminations can induce unique mechanical effects like crumpling at the nanosheet level [90]. Besides, the electrodes and electrolyte must work in unison to salvage the maximum possible charge storage ability.

Recently, Li-air batteries have experienced a resurgence due to the technological progress in preparing newer stable materials, the corresponding mechanistic understanding of such systems and the promising theoretical energy density of 3458 Wh kg^{-1}. Theoretically, MXene is an attractive cathode for Li-air batteries [117, 123], but so far, there seem to be no experiments reported, reaping the benefits of these theoretical guides [124]. Therefore, this direction is particularly attractive. And there is no reason to stop at Li-air batteries. Recent, studies on Zn-air batteries using MXene-based electrodes (figures 7(c) and (d)) are proof that this is a direction worth pursuing [116].

Operando characterization of batteries have already proven to be beneficial in understanding sodium and potassium ion battery mechanisms in MXene-based electrodes. For example, operando XRD studies have revealed the superior ability of MXene's (111) plane to accommodate large Na ions by showing no change over cycles but a pseudocapacitive intercalation mechanism could be guessed based on the (200) plane evolution (figures 7(e) and (f)) [118]. Since there are a large number of theoretical studies on multi-valent (e.g. Zn^{2+}, Mg^{2+}, Ca^{2+}, Al^{3+}) ion batteries with MXene-based electrodes but the performance is not as good as predicted, it is reasonable to assume a gap in fundamental understanding of mechanism. This gap must be closed by using in-operando characterization techniques to identify the problems and sought

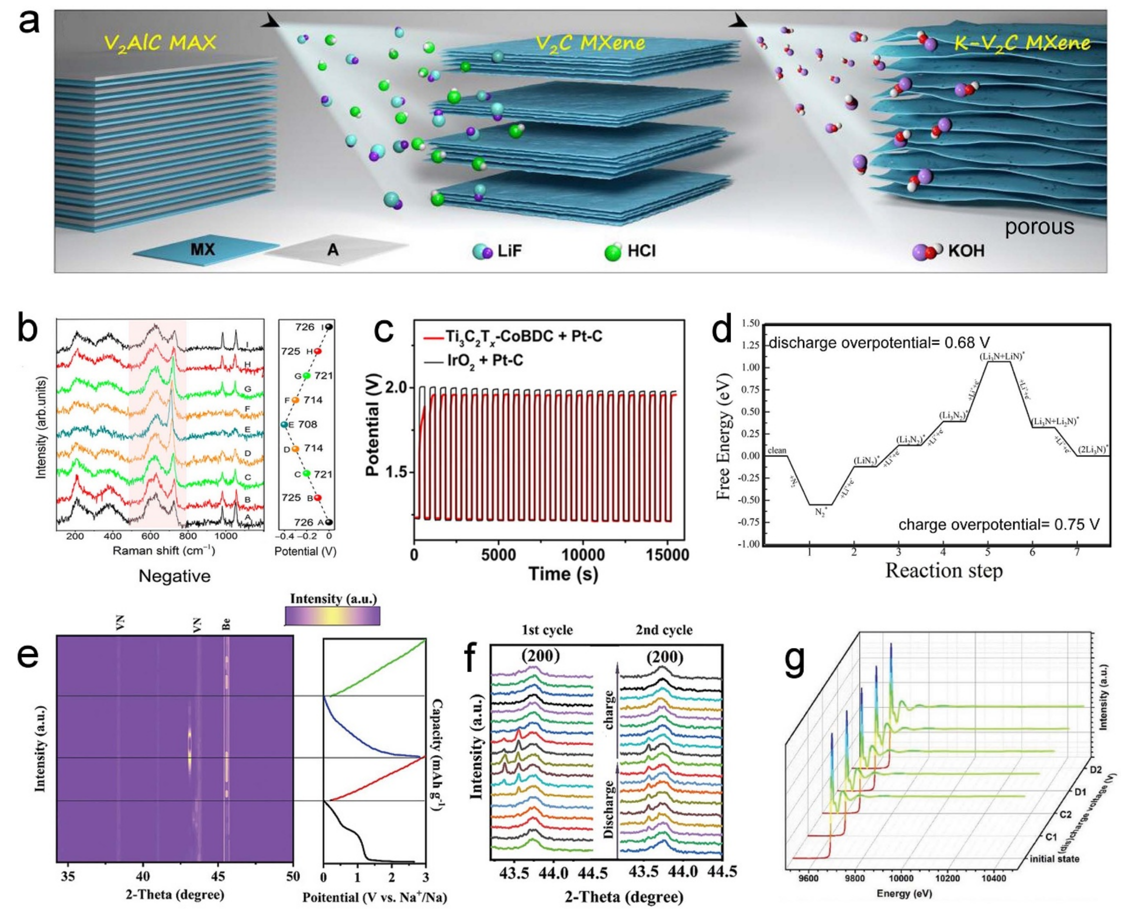

Figure 7. (a) Schematic showing the preparation of porous MXene using strong acid (LiF + HCl) and subsequent KOH treatment. (b) *In-situ* Raman spectra of MXene-based supercapacitor anode [62]. Copyright 2016, American Chemical Society. (c) GCD cycles of rechargeable Zn–air batteries with MXene-based electrodes at 0.8 mA cm^{-2} [116]. Copyright 2017, American Chemical Society. (d) Calculated energy profiles for formation of lithium nitride complex on lithiated MXene ($Ti_2CO_2Li_2$) under equilibrium potential suggesting the feasibility of Li-air battery using MXene electrodes [117]. Copyright 2019, Royal Society of Chemistry. (e) Operando x-ray diffraction (XRD) results during the first charge-discharge cycle of VN electrodes for Na ion battery. (f) Magnified view of the VN (200) plane evolution during the same cycling [118]. Copyright 2020, Wiley-VCH Verlag GmbH & Co. KgaA. (g) Evaluation of zinc hydroxide sulphate hydrate in zinc ion battery using operando XAFS [119]. Copyright 2019, Wiley-VCH Verlag GmbH & Co. KgaA.

suitable solutions. Research is advancing in this direction, evident from operando x-ray studies on hydrate precipitation having a stabilizing effect on Zn-ion supercapacitor with MXene-based electrodes (figure 7(g)). Therefore, we are hopeful such research will also benefit and encourage *in-situ* studies on multivalent ion batteries.

Most of the demonstrations of batteries using MXene have been done in coin-cells, naturally, because the primary focus is on characterizing the electrochemical properties of the active material. However, in the future it will become necessary to assemble pouch-type batteries/supercapacitors and integrate the batteries/supercapacitors with flexible or wearable devices. Therefore, we should be prepared for that, by growing the inventory of solid-state electrolytes that can complement the excellent properties of MXene-based flexible electrodes.

In one sentence, MXene's worth as a reliable electrode for electrochemical energy storage devices has been proven by tackling various obstacles and this trend is expected to continue in the future. Therefore, we are hopeful that MXene will realize its true potential by bringing 2D materials to the industrial-scale application.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (Grants 51872283, 21805273), National Key R&D Program of China (Grants 2016YFB0100100, 2016YFA0200200), LiaoNing Revitalization Talents Program (Grant XLYC1807153), Natural Science Foundation of Liaoning Province, Joint Research Fund Liaoning-Shenyang National Laboratory for Materials Science (Grant 20180510038), DICP (DICP ZZBS201708, DICP ZZBS201802), DICP&QIBEBT (Grant DICP&QIBEBT UN201702), Dalian National Laboratory For Clean Energy (DNL), CAS, DNL Cooperation Fund, CAS (DNL180310, DNL180308, DNL201912, DNL201915). P Das is grateful to the CAS-TWAS President's Fellowship (Fellowship No. 2017CTF018)

ORCID iDs

Prateek Das https://orcid.org/0000-0001-5185-950X
Zhong-Shuai Wu https://orcid.org/0000-0003-1851-4803

References

[1] Naguib M, Halim J, Lu J, Cook K M, Hultman L, Gogotsi Y and Barsoum M W 2013 New two-dimensional niobium and vanadium carbides as promising materials for Li-ion batteries *J. Am. Chem. Soc.* **135** 15966–9
[2] Okubo M, Sugahara A, Kajiyama S and Yamada A 2018 MXene as a charge storage host *Acc. Chem. Res.* **51** 591–9
[3] Wang H, Wu Y, Yuan X, Zeng G, Zhou J, Wang X and Chew J W 2018 Clay-inspired MXene-based electrochemical devices and photo-electrocatalyst: state-of-the-art progresses and challenges *Adv. Mater.* **30** 1704561
[4] Lei J-C, Zhang X and Zhou Z 2015 Recent advances in MXene: preparation, properties, and applications *Front. Phys.* **10** 276–86
[5] An H, Habib T, Shah S, Gao H, Radovic M, Green M J and Lutkenhaus J L 2018 Surface-agnostic highly stretchable and bendable conductive MXene multilayers *Sci. Adv.* **4** eaaq0118
[6] Dall'Agnese Y, Lukatskaya M R, Cook K M, Taberna P-L, Gogotsi Y and Simon P 2014 High capacitance of surface-modified 2D titanium carbide in acidic electrolyte *Electrochem. Commun.* **48** 118–22
[7] Hart J L, Hantanasirisakul K, Lang A C, Anasori B, Pinto D, Pivak Y, van Omme J T, May S J, Gogotsi Y and Taheri M L 2019 Control of MXenes' electronic properties through termination and intercalation *Nat. Commun.* **10** 522
[8] Khazaei M, Ranjbar A, Arai M, Sasaki T and Yunoki S 2017 Electronic properties and applications of MXenes: a theoretical review *J. Mater. Chem.* A **5** 2488–503
[9] Maleski K, Mochalin V N and Gogotsi Y 2017 Dispersions of two-dimensional titanium carbide MXene in organic solvents *Chem. Mater.* **29** 1632–40
[10] Wang Y, Wang X, Li X, Bai Y, Xiao H, Liu Y, Liu R and Yuan G 2019 Engineering 3D ion transport channels for flexible MXene films with superior capacitive performance *Adv. Funct. Mater.* **29** 1900326
[11] Zhan C, Naguib M, Lukatskaya M, Kent P R C, Gogotsi Y and D-e J 2018 Understanding the MXene pseudocapacitance *J. Phys. Chem. Lett.* **9** 1223–8
[12] Xiong D, Li X, Bai Z and Lu S 2018 Recent advances in layered $Ti_3C_2T_x$ MXene for electrochemical energy storage *Small* **14** 1703419
[13] Kajiyama S, Szabova L, Sodeyama K, Iinuma H, Morita R, Gotoh K, Tateyama Y, Okubo M and Yamada A 2016 Sodium-ion intercalation mechanism in MXene nanosheets *ACS Nano* **10** 3334–41
[14] Vonlanthen D, Lazarev P, See K A, Wudl F and Heeger A J 2014 A stable polyaniline-benzoquinone-hydroquinone supercapacitor *Adv. Mater.* **26** 5095–100
[15] Boota M and Gogotsi Y 2019 MXene—conducting polymer asymmetric pseudocapacitors *Adv. Energy Mater.* **9** 1802917
[16] Dong Y, Wu Z-S, Zheng S, Wang X, Qin J, Wang S, Shi X and Bao X 2017 Ti_3C_2 MXene-derived sodium/potassium titanate nanoribbons for high-performance sodium/potassium ion batteries with enhanced capacities *ACS Nano* **11** 4792–800
[17] Anasori B *et al* 2015 Two-dimensional, ordered, double transition metals carbides (MXenes) *ACS Nano* **9** 9507–16
[18] Zhang C *et al* 2018 Stamping of flexible, coplanar micro-supercapacitors using MXene inks *Adv. Funct. Mater.* **28** 1705506
[19] Kurra N, Ahmed B, Gogotsi Y and Alshareef H N 2016 MXene-on-paper coplanar microsupercapacitors *Adv. Energy Mater.* **6** 1601372
[20] Xu S, Dall'Agnese Y, Wei G, Zhang C, Gogotsi Y and Han W 2018 Screen-printable microscale hybrid device based on Mxene and layered double hydroxide electrodes for powering force sensors *Nano Energy* **50** 479–88
[21] Zhang C *et al* 2019 Additive-free MXene inks and direct printing of micro-supercapacitors *Nat. Commun.* **10** 1795
[22] Jiao S, Zhou A, Wu M and Hu H 2019 Kirigami patterning of MXene/bacterial cellulose composite paper for all-solid-state stretchable micro-supercapacitor arrays *Adv. Sci.* **6** 1900529
[23] Orangi J, Hamade F, Davis V A and Beidaghi M 2020 3D printing of additive-free 2D $Ti_3C_2T_x$ (MXene) ink for fabrication of micro-supercapacitors with ultra-high energy densities *ACS Nano* **14** 640–50
[24] Yang W, Yang J, Byun J J, Moissinac F P, Xu J, Haigh S J, Domingos M, Bissett M A, Dryfe R A W and Barg S 2019 3D printing of freestanding MXene architectures for current-collector-free supercapacitors *Adv. Mater.* **31** 1902725
[25] Tao Q *et al* 2017 Two-dimensional $Mo_{1.33}C$ MXene with divacancy ordering prepared from parent 3D laminate with in-plane chemical ordering *Nat. Commun.* **8** 14949
[26] Ling Z *et al* 2014 Flexible and conductive MXene films and nanocomposites with high capacitance *Proc. Natl. Acad. Sci. U. S. A.* **111** 16676–81
[27] González A, Goikolea E, Barrena J A and Mysyk R 2016 Review on supercapacitors: technologies and materials *Renew. Sustain. Energy Rev.* **58** 1189–206
[28] Lukatskaya M R, Mashtalir O, Ren C E, Dall'Agnese Y, Rozier P, Taberna P L, Naguib M, Simon P, Barsoum M W and Gogotsi Y 2013 Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide *Science* **341** 1502–5
[29] Das P, Shi X, Fu Q and Wu Z-S 2020 Substrate-free and shapeless planar micro-supercapacitors *Adv. Funct. Mater.* **30** 1908758
[30] Zhu Y *et al* 2011 Carbon-based supercapacitors produced by activation of graphene *Science* **332** 1537–41
[31] Solis-Fernandez P, Bissett M and Ago H 2017 Synthesis, structure and applications of graphene-based 2D heterostructures *Chem. Soc. Rev.* **46** 4572–613
[32] Ghidiu M, Lukatskaya M R, Zhao M-Q, Gogotsi Y and Barsoum M W 2014 Conductive two-dimensional titanium carbide 'clay' with high volumetric capacitance *Nature* **516** 78–81
[33] Lukatskaya M R *et al* 2017 Ultra-high-rate pseudocapacitive energy storage in two-dimensional transition metal carbides *Nat. Energy* **2** 17105
[34] Xu C, Wang H, Deng J and Wang Y 2018 High-performance flexible redox supercapacitors induced by methylene blue with a wide voltage window *Sustain. Energy Fuels* **2** 357–60

[35] Gund G S, Park J H, Harpalsinh R, Kota M, Shin J H, T-i K, Gogotsi Y and Park H S 2019 MXene/polymer hybrid materials for flexible AC-filtering electrochemical capacitors *Joule* **3** 164–76
[36] Tang X, Guo X, Wu W and Wang G 2018 2D metal carbides and nitrides (MXenes) as high-performance electrode materials for lithium-based batteries *Adv. Energy Mater.* **8** 1801897
[37] Li X, Wang C, Cao Y and Wang G 2018 Functional MXene materials: progress of their applications *Chem. Asian J.* **13** 2742–57
[38] Fatima M, Fatheema J, Monir N B, Siddique A H, Khan B, Islam A, Akinwande D and Rizwan S 2020 Nb-doped MXene with enhanced energy storage capacity and stability *Front. Chem.* **8** 168
[39] Luo J *et al* 2019 Atomic sulfur covalently engineered interlayers of Ti_3C_2 MXene for ultra-fast sodium-ion storage by enhanced pseudocapacitance *Adv. Funct. Mater.* **29** 1808107
[40] Luo J *et al* 2017 Pillared structure design of MXene with ultralarge interlayer spacing for high-performance lithium-ion capacitors *ACS Nano* **11** 2459–69
[41] Luo J, Tao X, Zhang J, Xia Y, Huang H, Zhang L, Gan Y, Liang C and Zhang W 2016 Sn^{4+} ion decorated highly conductive Ti_3C_2 MXene: promising lithium-ion anodes with enhanced volumetric capacity and cyclic performance *ACS Nano* **10** 2491–9
[42] Yang C, Que W, Tang Y, Tian Y and Yin X 2017 Nitrogen and sulfur Co-doped 2D titanium carbides for enhanced electrochemical performance *J. Electrochem. Soc.* **164** A1939–45
[43] Pan Z and Ji X 2019 Facile synthesis of nitrogen and oxygen co-doped C@ Ti_3C_2 MXene for high performance symmetric supercapacitors *J. Power Sources* **439** 227068
[44] Yoon Y, Lee M, Kim S K, Bae G, Song W, Myung S, Lim J, Lee S S, Zyung T and An K-S 2018 A strategy for synthesis of carbon nitride induced chemically doped 2D MXene for high-performance supercapacitor electrodes *Adv. Energy Mater.* **8** 1703173
[45] Wang X *et al* 2019 Influences from solvents on charge storage in titanium carbide MXenes *Nat. Energy* **4** 241–8
[46] Gogotsi Y and Anasori B 2019 The rise of MXenes *ACS Nano* **13** 8491–4
[47] Kim K, Ando Y, Sugahara A, Ko S, Yamada Y, Otani M, Okubo M and Yamada A 2019 Dense charge accumulation in MXene with a hydrate-melt electrolyte *Chem. Mater.* **31** 5190–6
[48] Kim K, Okubo M and Yamada A 2019 Interfacial dissociation of contact-ion-pair on MXene electrodes in concentrated aqueous electrolytes *J. Electrochem. Soc.* **166** A3739–44
[49] Zheng S, Zhang C, Zhou F, Dong Y, Shi X, Nicolosi V, Wu Z-S and Bao X 2019 Ionic liquid pre-intercalated MXene films for ionogel-based flexible micro-supercapacitors with high volumetric energy density *J. Mater. Chem.* A **7** 9478–85
[50] Lin Z, Barbara D, Taberna P-L, Van Aken K L, Anasori B, Gogotsi Y and Simon P 2016 Capacitance of $Ti_3C_2T_x$ MXene in ionic liquid electrolyte *J. Power Sources* **326** 575–9
[51] Zhao F, Liu W, Qiu T, Gong W-B, Ma W, Li Q, Li F and Geng F 2020 All two-dimensional pseudocapacitive sheet materials for flexible asymmetric solid-state planar microsupercapacitors with high energy density *ACS Nano* **14** 603–10
[52] Avireddy H *et al* 2019 Stable high-voltage aqueous pseudocapacitive energy storage device with slow self-discharge *Nano Energy* **64** 103961
[53] Zheng S *et al* 2019 All-solid-state planar sodium-ion microcapacitors with multidirectional fast ion diffusion pathways *Adv. Sci.* **6** 1902147
[54] Shi X, Zhou F, Peng J, Wu R, Wu Z-S and Bao X 2019 One-step scalable fabrication of graphene-integrated micro-supercapacitors with remarkable flexibility and exceptional performance uniformity *Adv. Funct. Mater.* **29** 1902860
[55] Zheng S, Shi X, Das P, Wu Z-S and Bao X 2019 The road towards planar microbatteries and micro-supercapacitors: from 2D to 3D device geometries *Adv. Mater.* **31** 1900583
[56] Das P, Fu Q, Bao X and Wu Z-S 2018 Recent advances in the preparation, characterization, and applications of two-dimensional heterostructures for energy storage and conversion *J. Mater. Chem.* A **6** 21747–84
[57] Jiang Q, Wu C, Wang Z, Wang A C, He J-H, Wang Z L and Alshareef H N 2018 MXene electrochemical microsupercapacitor integrated with triboelectric nanogenerator as a wearable self-charging power unit *Nano Energy* **45** 266–72
[58] Boota M, Anasori B, Voigt C, Zhao M-Q, Barsoum M W and Gogotsi Y 2016 Pseudocapacitive electrodes produced by oxidant-free polymerization of pyrrole between the layers of 2D titanium carbide (MXene) *Adv. Mater.* **28** 1517–22
[59] Xia Y, Mathis T S, Zhao M-Q, Anasori B, Dang A, Zhou Z, Cho H, Gogotsi Y and Yang S 2018 Thickness-independent capacitance of vertically aligned liquid-crystalline MXenes *Nature* **557** 409–12
[60] Li H, Hou Y, Wang F, Lohe M R, Zhuang X, Niu L and Feng X 2017 Flexible all-solid-state supercapacitors with high volumetric capacitances boosted by solution processable MXene and electrochemically exfoliated graphene *Adv. Energy Mater.* **7** 1601847
[61] Huang H *et al* 2019 Massively manufactured paper-based all-solid-state flexible micro-supercapacitors with sprayable MXene conductive inks *J. Power Sources* **415** 1–7
[62] Hu M M, Li Z J, Hu T, Zhu S H, Zhang C and Wang X H 2016 High-capacitance mechanism for $Ti_3C_2T_x$ MXene by *in situ* electrochemical Raman spectroscopy investigation *ACS Nano* **10** 11344–50
[63] Hu H and Hua T 2017 An easily manipulated protocol for patterning of Mxenes on paper for planar micro-supercapacitors *J. Mater. Chem.* A **5** 19639–48
[64] Yu L, Fan Z, Shao Y, Tian Z, Sun J and Liu Z 2019 Versatile N-doped MXene ink for printed electrochemical energy storage application *Adv. Energy Mater.* **9** 1901839
[65] Yue Y *et al* 2018 Highly self-healable 3D microsupercapacitor with MXene–graphene composite aerogel *ACS Nano* **12** 4224–32
[66] Zhou Y *et al* 2020 $Ti_3C_2T_x$ MXene-reduced graphene oxide composite electrodes for stretchable supercapacitors *ACS Nano* **14** 3576–86
[67] Huang Y, Zhong M, Huang Y, Zhu M, Pei Z, Wang Z, Xue Q, Xie X and Zhi C 2015 A self-healable and highly stretchable supercapacitor based on a dual crosslinked polyelectrolyte *Nat. Commun.* **6** 10310
[68] Zhang Y-Z, Lee K H, Anjum D H, Sougrat R, Jiang Q, Kim H and Alshareef H N 2018 MXenes stretch hydrogel sensor performance to new limits *Sci. Adv.* **4** eaat0098
[69] Zhang J, Wan L, Gao Y, Fang X, Lu T, Pan L and Xuan F 2019 Highly stretchable and self-healable MXene/polyvinyl alcohol hydrogel electrode for wearable capacitive electronic skin *Adv. Electron. Mater.* **5** 1900285
[70] Whittingham M S 2004 Lithium batteries and cathode materials *Chem. Rev.* **104** 4271–302
[71] Scrosati B 2011 History of lithium batteries *J. Solid. State Electrochem.* **15** 1623–30
[72] Gerdes J W, Gupta S K and Wilkerson S A 2012 A review of bird-inspired flapping wing miniature air vehicle designs *J. Mech. Robot.* **4** 021003
[73] Kim T, Song W, Son D-Y, Ono L K and Qi Y 2019 Lithium-ion batteries: outlook on present, future, and hybridized technologies *J. Mater. Chem.* A **7** 2942–64
[74] Tomaszewska A *et al* 2019 Lithium-ion battery fast charging: a review *eTransportation* **1** 100011

[75] Naguib M, Come J, Dyatkin B, Presser V, Taberna P-L, Simon P, Barsoum M W and Gogotsi Y 2012 MXene: a promising transition metal carbide anode for lithium-ion batteries *Electrochem. Commun.* **16** 61–64

[76] Tang Q, Zhou Z and Shen P 2012 Are MXenes promising anode materials for Li ion batteries? Computational studies on electronic properties and Li storage capability of Ti_3C_2 and $Ti_3C_2X_2$ (X = F, OH) monolayer *J. Am. Chem. Soc.* **134** 16909–16

[77] Kajiyama S, Szabova L, Iinuma H, Sugahara A, Gotoh K, Sodeyama K, Tateyama Y, Okubo M and Yamada A 2017 Enhanced Li-ion accessibility in MXene titanium carbide by steric chloride termination *Adv. Energy Mater.* **7** 1601873

[78] Dong Y, Zheng S, Qin J, Zhao X, Shi H, Wang X, Chen J and Wu Z-S 2018 All-MXene-based integrated electrode constructed by Ti_3C_2 nanoribbon framework host and nanosheet interlayer for high-energy-density Li–S batteries *ACS Nano* **12** 2381–8

[79] Shi H, Zhang C J, Lu P, Dong Y, Wen P and Wu Z-S 2019 Conducting and lithiophilic MXene/graphene framework for high-capacity, dendrite-free lithium–metal anodes *ACS Nano* **13** 14308–18

[80] Xie Y, Naguib M, Mochalin V N, Barsoum M W, Gogotsi Y, Yu X, Nam K-W, Yang X-Q, Kolesnikov A I and Kent P R C 2014 Role of surface structure on Li-ion energy storage capacity of two-dimensional transition-metal carbides *J. Am. Chem. Soc.* **136** 6385–94

[81] Fang R, Zhao S, Sun Z, Wang D-W, Cheng H-M and Li F 2017 More reliable lithium-sulfur batteries: status, solutions and prospects *Adv. Mater.* **29** 1606823

[82] Rana M, Luo B, Kaiser M R, Gentle I and Knibbe R 2020 The role of functional materials to produce high areal capacity lithium sulfur battery *J. Energy Chem.* **42** 195–209

[83] Fang M, Liu X, Ren J-C, Yang S, Su G, Fang Q, Lai J, Li S and Liu W 2020 Revisiting the anchoring behavior in lithium-sulfur batteries: many-body effect on the suppression of shuttle effect *Npj Comput. Mater.* **6** 8

[84] Hu L, Dai C, Lim J-M, Chen Y, Lian X, Wang M, Li Y, Xiao P, Henkelman G and Xu M 2018 A highly efficient double-hierarchical sulfur host for advanced lithium–sulfur batteries *Chem. Sci.* **9** 666–75

[85] Wang J *et al* 2019 Rational design of porous N-Ti_3C_2 MXene@CNT microspheres for high cycling stability in Li–S battery *Nanomicro. Lett.* **12** 4

[86] Lian P, Dong Y, Wu Z-S, Zheng S, Wang X, Sen W, Sun C, Qin J, Shi X and Bao X 2017 Alkalized Ti_3C_2 MXene nanoribbons with expanded interlayer spacing for high-capacity sodium and potassium ion batteries *Nano Energy* **40** 1–8

[87] Li N, Xie Y, Peng S, Xiong X and Han K 2020 Ultra-lightweight $Ti_3C_2T_x$ MXene modified separator for Li–S batteries: thickness regulation enabled polysulfide inhibition and lithium ion transportation *J. Energy Chem.* **42** 116–25

[88] Wang D, Li F, Lian R, Xu J, Kan D, Liu Y, Chen G, Gogotsi Y and Wei Y 2019 A general atomic surface modification strategy for improving anchoring and electrocatalysis behavior of $Ti_3C_2T_2$ MXene in lithium–sulfur batteries *ACS Nano* **13** 11078–86

[89] Song Y *et al* 2020 Rational design of porous nitrogen-doped Ti_3C_2 MXene as a multifunctional electrocatalyst for Li–S chemistry *Nano Energy* **70** 104555

[90] Bao W, Liu L, Wang C, Choi S, Wang D and Wang G 2018 Facile synthesis of crumpled nitrogen-doped MXene nanosheets as a new sulfur host for lithium–sulfur batteries *Adv. Energy Mater.* **8** 1702485

[91] Xiao Z, Li Z, Meng X and Wang R 2019 MXene-engineered lithium–sulfur batteries *J. Mater. Chem.* A **7** 22730–43

[92] Cheng X-B, Zhang R, Zhao C-Z and Zhang Q 2017 Toward safe lithium metal anode in rechargeable batteries: a review *Chem. Rev.* **117** 10403–73

[93] Kang K, Meng Y S, Bréger J, Grey C P and Ceder G 2006 Electrodes with high power and high capacity for rechargeable lithium batteries *Science* **311** 977–80

[94] Albertus P, Babinec S, Litzelman S and Newman A 2018 Status and challenges in enabling the lithium metal electrode for high-energy and low-cost rechargeable batteries *Nat. Energy* **3** 16–21

[95] Li P, Dong X, Li C, Liu J, Liu Y, Feng W, Wang C, Wang Y and Xia Y 2019 Anchoring an artificial solid–electrolyte interphase layer on a 3D current collector for high-performance lithium anodes *Angew. Chem. Int. Ed.* **58** 2093–7

[96] Cha E, Patel M D, Park J, Hwang J, Prasad V, Cho K and Choi W 2018 2D MoS_2 as an efficient protective layer for lithium metal anodes in high-performance Li–S batteries *Nat. Nanotechnol.* **13** 337–44

[97] Yang C, Yao Y, He S, Xie H, Hitz E and Hu L 2017 Ultrafine silver nanoparticles for seeded lithium deposition toward stable lithium metal anode *Adv. Mater.* **29** 1702714

[98] Gu J, Zhu Q, Shi Y, Chen H, Zhang D, Du Z and Yang S 2020 Single zinc atoms immobilized on MXene ($Ti_3C_2Cl_x$) layers toward dendrite-free lithium metal anodes *ACS Nano* **14** 891–8

[99] Xie Y, Dall'Agnese Y, Naguib M, Gogotsi Y, Barsoum M W, Zhuang H L and Kent P R C 2014 Prediction and characterization of MXene nanosheet anodes for non-lithium-ion batteries *ACS Nano* **8** 9606–15

[100] Er D, Li J, Naguib M, Gogotsi Y and Shenoy V B 2014 Ti_3C_2 MXene as a high capacity electrode material for metal (Li, Na, K, Ca) ion batteries *ACS Appl. Mater. Interfaces* **6** 11173–9

[101] Zhao R, Qian Z, Liu Z, Zhao D, Hui X, Jiang G, Wang C and Yin L 2019 Molecular-level heterostructures assembled from layered black phosphorene and Ti_3C_2 MXene as superior anodes for high-performance sodium ion batteries *Nano Energy* **65** 104037

[102] Li H, Liu A, Ren X, Yang Y, Gao L, Fan M and Ma T 2019 A black phosphorus/Ti_3C_2 MXene nanocomposite for sodium-ion batteries: a combined experimental and theoretical study *Nanoscale* **11** 19862–9

[103] Guo X, Xie X, Choi S, Zhao Y, Liu H, Wang C, Chang S and Wang G 2017 Sb_2O_3/MXene($Ti_3C_2T_x$) hybrid anode materials with enhanced performance for sodium-ion batteries *J. Mater. Chem.* A **5** 12445–52

[104] Zhu J and Schwingenschlögl U 2017 P and Si functionalized MXenes for metal-ion battery applications *2D Mater.* **4** 025073

[105] Meng Q, Ma J, Zhang Y, Li Z, Zhi C, Hu A and Fan J 2018 The S-functionalized Ti_3C_2 MXene as a high capacity electrode material for Na-ion batteries: a DFT study *Nanoscale* **10** 3385–92

[106] Zhao R, Di H, Hui X, Zhao D, Wang R, Wang C and Yin L 2020 Self-assembled Ti_3C_2 MXene and N-rich porous carbon hybrids as superior anodes for high-performance potassium-ion batteries *Energy Environ. Sci.* **13** 246–57

[107] Li Y, Deng Y, Zhang J, Han Y, Zhang W, Yang X, Zhang X and Jiang W 2019 Tunable energy storage capacity of two-dimensional $Ti_3C_2T_x$ modified by a facile two-step pillaring strategy for high performance supercapacitor electrodes *Nanoscale* **11** 21981–9

[108] VahidMohammadi A, Hadjikhani A, Shahbazmohamadi S and Beidaghi M 2017 Two-dimensional vanadium carbide (MXene) as a high-capacity cathode material for rechargeable aluminum batteries *ACS Nano* **11** 11135–44

[109] Huo X, Wang X, Li Z, Liu J and Li J 2020 Two-dimensional composite of D-$Ti_3C_2T_x$@S@TiO_2 (MXene) as the cathode material for aluminum-ion batteries *Nanoscale* **12** 3387–99

[110] Luo S, Xie L, Han F, Wei W, Huang Y, Zhang H, Zhu M, Schmidt O G and Wang L 2019 Nanoscale parallel circuitry based on interpenetrating conductive assembly for flexible and high-power zinc ion battery *Adv. Funct. Mater.* **29** 1901336

[111] Li X *et al* 2020 Phase transition induced unusual electrochemical performance of V_2CT_X MXene for aqueous zinc hybrid-ion battery *ACS Nano* **14** 541–51

[112] Eames C and Islam M S 2014 Ion intercalation into two-dimensional transition-metal carbides: global screening for new high-capacity battery materials *J. Am. Chem. Soc.* **136** 16270–6

[113] Greaves M, Barg S and Bissett M A 2019 MXene-based anodes for metal-ion batteries *Batteries Supercaps* **3** 214–35

[114] Hong X, Mei J, Wen L, Tong Y, Vasileff A J, Wang L, Liang J, Sun Z and Dou S X 2019 Nonlithium metal–sulfur batteries: steps toward a leap *Adv. Mater.* **31** 1802822

[115] Dall'Agnese Y, Taberna P-L, Gogotsi Y and Simon P 2015 Two-dimensional vanadium carbide (MXene) as positive electrode for sodium-ion capacitors *J. Phys. Chem. Lett.* **6** 2305–9

[116] Zhao L *et al* 2017 Interdiffusion reaction-assisted hybridization of two-dimensional metal–organic frameworks and $Ti_3C_2T_x$ nanosheets for electrocatalytic oxygen evolution *ACS Nano* **11** 5800–7

[117] Yi S, Liu G, Liu Z, Hu W and Deng H 2019 Theoretical insights into nitrogen fixation on Ti_2C and Ti_2CO_2 in a lithium–nitrogen battery *J. Mater. Chem.* A **7** 19950–60

[118] Wei S, Wang C, Chen S, Zhang P, Zhu K, Wu C, Song P, Wen W and Song L 2020 Dial the mechanism switch of VN from conversion to intercalation toward long cycling sodium-ion battery *Adv. Energy Mater.* 1903712

[119] Wang C, Wei S, Chen S, Cao D and Song L 2019 Delaminating vanadium carbides for zinc-ion storage: hydrate precipitation and H^+/Zn^{2+} Co-action mechanism *Small Methods* **3** 1900495

[120] Ming F, Liang H, Zhang W, Ming J, Lei Y, Emwas A-H and Alshareef H N 2019 Porous MXenes enable high performance potassium ion capacitors *Nano Energy* **62** 853–60

[121] Wang X, Kajiyama S, Iinuma H, Hosono E, Oro S, Moriguchi I, Okubo M and Yamada A 2015 Pseudocapacitance of MXene nanosheets for high-power sodium-ion hybrid capacitors *Nat. Commun.* **6** 6544

[122] Zhong J, Sun W, Wei Q, Qian X, Cheng H-M and Ren W 2018 Efficient and scalable synthesis of highly aligned and compact two-dimensional nanosheet films with record performances *Nat. Commun.* **9** 3484

[123] Ostadhossein A, Guo J, Simeski F and Ihme M 2019 Functionalization of 2D materials for enhancing OER/ORR catalytic activity in Li–oxygen batteries *Commun. Chem.* **2** 95

[124] Yang Y, Yao M, Wang X and Huang H 2019 Theoretical prediction of catalytic activity of Ti_2C MXene as cathode for $Li–O_2$ batteries *J. Phys. Chem.* C **123** 17466–71