Zhang, Chuanfang (John); Cui, Linfan; Abdolhosseinzadeh, Sina; Heier, Jakob

Two-dimensional MXenes for lithium-sulfur batteries

Published in:
InfoMat

DOI:
10.1002/inf2.12080

Published: 01/07/2020

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
CC BY

Please cite the original version:
Two-dimensional MXenes for lithium-sulfur batteries

Chuanfang (John) Zhang1 | Linfan Cui2 | Sina Abdolhosseinzadeh1,3 | Jakob Heier1

1Laboratory for Functional Polymers, Empa, Swiss Federal Laboratories for Materials Science and Technology, Dübendorf, Switzerland
2Department of Electronics and Nanoengineering, Aalto University, Aalto, Finland
3Institute of Materials Science and Engineering, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland

Correspondence
Chuanfang (John) Zhang, Laboratory for Functional Polymers, Empa, Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland.
Email: chuanfang.zhang@empa.ch

Abstract
Rechargeable lithium-sulfur (Li-S) batteries have attracted significant research attention due to their high capacity and energy density. However, their commercial applications are still hindered by challenges such as the shuttle effect of soluble lithium sulfide species, the insulating nature of sulfur, and the fast capacity decay of the electrodes. Various efforts are devoted to address these problems through questing more conductive hosts with abundant polysulfide chemisorption sites, as well as modifying the separators to physically/chemically retard the polysulfides migration. Two dimensional transition metal carbides, carbonitrides and nitrides, so-called MXenes, are ideal for confining the polysulfides shuttling effects due to their high conductivity, layered structure as well as rich surface terminations. As such, MXenes have thus been widely studied in Li-S batteries, focusing on the conductive sulfur hosts, polysulfides interfaces, and separators. Therefore, in this review, we summarize the significant progresses regarding the design of multifunctional MXene-based Li-S batteries and discuss the solutions for improving electrochemical performances in detail. In addition, challenges and perspectives of MXenes for Li-S batteries are also outlined.

KEYWORDS
flexible electronics, Li-S battery, MXene, polysulfides, shuttling, two dimensional materials

1 INTRODUCTION

The great demands for portable electronics and the emergence of electric vehicles have significantly stimulated the developments of energy-storage devices.1-4 Comparing to Li-ion batteries and other metal-sulfur batteries, lithium-sulfur (Li-S) battery is considered as one of the promising electrical energy storage systems owing to the natural abundance of sulfur, high theoretical specific capacity (1675 mA h g⁻¹) and energy density (~2670 W h kg⁻¹),5-8 as shown in Figure 1A. However, the soluble long chain lithium polysulfides (Li₂Sₙ, 4 ≤ n ≤ 8) produced in the discharge process disassociate into electrolyte and shuttle between cathode and anode (Figure 1B), typically known as the shuttling effect.6,7 This effect results in active material loss, causing rapid capacity decay, low cyclic performance and Coulombic efficiency. The Li₂Sₙ also reacts with the Li anode and forms an insulating layer, leading to serious polarization. In the meanwhile, the insulating nature of sulfur greatly lowers down the redox reaction...
kinetics, thus reducing the rate capabilities and sulfur utilization. All of these abovementioned issues urgently require effective conductive hosts or separators to suppress the polysulfide migration process. In general, methods can be classified as physically confinements and chemically adsorption of the Li$_2$Sn. For instance, carbon materials with high specific surface area and rich porosity provide effective physical confinements of Li$_2$Sn, leading to dramatically improved long-term cycling. A conductive polymer matrix can also help to encapsulate sulfur in the cathode and achieve good capacity and cycling performance. Graphene oxides with abundant surface functional groups, as well as the hydrophilic metal oxides on the other hand, trap the polysulfide diffusion through a chemical adsorption mechanism.

Since the discovery of Ti$_3$C$_2$Tx in 2011, transition metal carbides and nitrides, so-called MXenes, have attracted extensive attention and exhibited excellent performances in energy, catalysis, optoelectronics, biomedical, environment, sensors, electromagnetic fields and so on (Figure 1C). MXenes with formula M$_{n+1}$X$_n$Tx ($n = 1$-$3$) are usually derived from the parental MAX phases by selectively etching the A layer (where M represents a transition metal, A represents the group 13 or 14 elements in the periodic table and X represents carbon or nitrogen, T$_x$ stands for the surface terminations). Thus, the obtained MXenes possess a unique layered structure. After etching, the surface of MXenes is terminated with various functional groups such as hydroxyl (−OH), oxygen (−O), chlorine (−Cl) and fluorine (−F), leading to a good hydrophilicity in MXenes which is in sharp contrast with hydrophobic graphene nanosheets. Beyond the excellent electronic conductivity, MXenes have also exhibited impressive performances in many areas, especially in energy storage. Thus, the past few years have witnessed the rise of MXenes, best evidenced by the ever-increasing number of publications on this new class of two-dimensional (2D) wonder materials (Figure 1D). Particular attention should be paid to the application of MXenes in Li-S batteries. The surface groups on MXenes (especially hydroxyl groups) are highly affinitive to polysulfides and can spontaneously attract them without additional surface modifications. Moreover, the highly conductive core (Ti−C−Ti bonds) can greatly facilitate the charge transfer kinetics, allowing great enhancement of sulfur utilization and cell rate handling as a result. Said otherwise, using MXenes as sulfur conductive host and/or modified

---

**FIGURE 1** A, Comparison of energy densities of various metal-sulfur batteries. B, Schematic illustration of working mechanism of Li-S batteries. C, Explored applications of MXenes. Images are from the internet. D, The number of publications on MXene and E, MXene-based Li-S batteries (Source: Web of Science)
separator can dramatically boost the long-term cycling and capacity of the assembled Li-S cells.

As a matter of fact, publications on the MXenes for Li-S batteries also increase apparently, suggesting this field gets more and more research attention (Figure 1E). As such, it is important to summarize the significant progresses covering the topics like conductive hosts, high sulfur loading, modified separators, as well as the theoretical simulations and calculations, and so forth. Herein, we review the recent progresses of MXenes for Li-S batteries. We especially focus on the structural design of the MXene-S electrode, as well as solutions for boosting the electrode/device performances. We also revisit the theoretical calculations based on density-functional theories (DFT) to simulate the interactions between MXenes and polysulfides. Finally, we present the challenge of MXenes for the Li-S batteries and outlook the future possible solutions to these challenges.

## 2 | MXENE: SYNTHESIS AND PROPERTIES

### 2.1 | Synthesis of MXenes

As the first discovered MXene, Ti$_3$C$_2$Tx is produced by a wet-chemical etching process from MAX phase (Figure 2A).$^{16,18,19,21,24,25}$ In this method, the etchant, typically aqueous hydrofluoric acid (HF), selectively etches away the A atomic layer from the MAX precursor as the M-A bond is more chemically active than the M-X bond. After etching, the solids are repeatedly washed with deionized water followed by centrifugation till the pH of the supernatant reaches 4-6, and multilayered (m-) Ti$_3$C$_2$Tx MXene is obtained. Similarly, by adjusting the HF etching conditions such as HF concentration, etching time and temperature, other types of MXenes, such as Ti$_2$CT$_x$, Ti$_3$CNT$_x$, Nb$_2$CT$_x$ and V$_2$CT$_x$ have also been synthesized.$^{16,26,27}$

In order to obtain individual 2D MXene nanosheets, delamination of the m-Ti$_3$C$_2$Tx is necessary. This can be done by intercalating polar organic molecules such as hydrazine, urea, dimethyl sulfoxide (DMSO) and isopropylamine into the m-Ti$_3$C$_2$Tx, followed by sonication to delaminate the sheets.$^{28,29}$ In order to increase the yield of delaminated nanosheets, organic intercalants with large cation size, such as tetrabutylammonium hydroxide (TBAOH), choline hydroxide or n-butylamine, are used to give large amounts of delaminated nanosheet solutions, as shown in Figure 2B,C.$^{30}$ After mechanical vibration or sonication in water, single or few-layer MXene solutions can be collected.

Unlike the HF acid etching, using lithium fluoride (LiF) and hydrochloric acid (HCl) mixture to produce HF in-situ can effectively etch away the A layer and result in Ti$_3$C$_2$Tx MXene with Li ion (Li$^+$) pre-intercalated in the layered solids. Consequently, by repeated ion exchanging (through DI-water washing) and manual shaking/sonication, delaminated nanosheets, with predominantly mono-layered flakes enriched in the solution, can be effectively

---

prepared.\textsuperscript{21,32} Compared to the nanosheets produced via direct HF etching, the flakes prepared from the LiF-HCl route possess a cleaner surface with much less defects, and thus termed as minimally intensive layer delamination (MILD) route.\textsuperscript{33,34} Ti$_3$C$_2$Tx MXene can also be produced upon etching in the ammonium bifluoride salt (NH$_4$HF$_2$).\textsuperscript{35} Similarly, using molten salts, that is, KF, LiF, NaF is another route to effectively etch away the A layer and produce good quality MXenes.\textsuperscript{36}

Nevertheless, the abovementioned etching-delamination routes produce Ti$_3$C$_2$Tx nanosheet solutions at a low yield, typically <20%. To boost the yield of nanosheets, other novel methods such as electro-chemical etching and microwave-assisted delamination strategies have been developed.\textsuperscript{37,38} During the electro-chemical etching process, Ti$_3$AlC$_2$ can be etched in the Cl$^-$/ containing electrolyte under a low potential as Cl$^-$ has a strong binding capability with Al. The microwave-assisted delamination strategy utilizes an agitation-intercalation-exfoliation process with organic solvent/ionic liquid media to break the interactions among the Ti$_3$C$_2$T$_x$ nanosheets.

In particular, through employing a hydrothermal-assisted interaction strategy, the yield of Ti$_3$C$_2$T$_x$ sheets can achieve 74% (Figure 3A).\textsuperscript{39} In this process, the intercalation process is facilitated under the hydrothermal conditions, thus promoting the delamination yield. On the other side, as the HF acid is highly corrosive, other safer strategies, such as alkali-etching method has also been emerged to obtain Ti$_3$C$_2$T$_x$ (Figure 3B).\textsuperscript{40}

While the wet-chemistry method is able to efficiently synthesize carbide MXenes, it is quite challenging to prepare nitride MXenes using this method. Instead, nitride MXenes can be fabricated by high temperature etching of the MAX phase. A typical example is the synthesis of Ti$_4$N$_3$T$_x$, which was obtained by etching the Ti$_4$AlN$_3$ MAX phase in a molten fluoride salt mixture under 550°C in argon atmosphere (Figure 3C).\textsuperscript{36} By ammonization of the carbide MXene (ie, Mo$_2$CT$_x$ and V$_2$CT$_x$) at 600°C, corresponding Mo$_2$NT$_x$ and V$_2$NT$_x$ (mixed with cubic VN) MXenes can be effectively prepared.\textsuperscript{42} Nevertheless, the production yield of nitride MXenes is low based on the ammonization of carbide MXene route. Said otherwise, more efficient routes to the nitride MXene synthesis are greatly in need to continuously expand the MXene family.

In addition, carbides with double or triple A layers have also been selected as precursors to synthesize MXenes.\textsuperscript{43,44} Mo$_2$CT$_x$ can be prepared from Mo$_2$Ga$_2$C by etching two A-element layers while Zr$_3$C$_2$T$_x$ is synthesized from Zr$_3$Al$_3$C$_5$ by etching Al$_2$C$_3$.\textsuperscript{44} On the other hand, molybdenum carbide with large lateral size and less defects can also be prepared through a chemical vapor deposition (CVD) method.\textsuperscript{41} As shown in Figure 3D, ultrathin α-Mo$_2$C has been produced through CVD on a copper foil which was placed on a molybdenum foil. During the

**FIGURE 3** A, Schematic of hydrothermal-assisted intercalation strategy to synthesize Ti$_3$C$_2$T$_x$. Reproduced with permission.\textsuperscript{39} Copyright 2019, American Chemical Society. B, Schematic of fluorine-free etching method to synthesize MXene via the reaction between Ti$_3$AlC$_2$ and NaOH water solution under different conditions. Reproduced with permission.\textsuperscript{40} Copyright 2018, Wiley-VCH. C, Synthesis process of Ti$_4$N$_3$T$_x$ using a high temperature etching method. Reproduced with permission.\textsuperscript{36} Copyright 2016, The Royal Society of Chemistry. D, Schematic of the synthesis process of α-Mo$_2$C crystals via CVD method. Reproduced with permission.\textsuperscript{41} Copyright 2015, Wiley-VCH
reaction, the Mo atoms diffuse to the top Cu surface and combine with the decomposed carbon atoms, forming \( \alpha \)-Mo\(_2\)C nuclei which grow continuously along the epitaxial direction. As a result, the \( \alpha \)-Mo\(_2\)C flakes are of high quality, allowing the investigation of their intrinsic properties such as electrical, mechanical and optoelectronic properties.\(^{41,45}\)

### 2.2 Properties of MXenes

MXene crystals possess a hexagonal close-packed stacking structure where M atoms are closely packed and X atoms fill the octahedral interstitial sites.\(^{21}\) The MXene family usually has three packing configurations, that is, \( M_2X \), \( M_3X_2 \) and \( M_4X_3 \) with the corresponding single sheets of 3, 5, 7 layers, rendering the great diversity of the MXene family (Figure 4A). Recently, Anasori et al reported the ordered double transition metal MXenes, where one (or two) transition metal layer(s) is (are) sandwiched between the second transition metal layers (as shown in Figure 4B).\(^{25}\) Such an atomic structure is totally different from the solid-state solutions MXenes, where the different metal atoms are distributed randomly. The discovery of the ordered double transition metal MXenes have greatly enriched the MXene family, opening up new possibilities in tuning the band gap, work function, and optoelectronic properties of MXenes.

Typically, MXenes synthesized via HF or HF-containing solution possess abundant hydrophilic surface functional groups (\(-\text{OH}, -\text{O}, \text{and} -\text{F}\)). In order to modify the surface groups, especially to produce MXenes with reduced surface functionalities, annealing MXenes under argon (Ar) has been proved to be quite effective.\(^{46}\) For example, by annealing the Ti\(_3\)C\(_2\)Tx MXene in Ar at 500°C, most of the surface groups can be removed. It is quite challenging to produce MXenes with one specific surface group. Nevertheless, many studies assume that MXene possess only one type of surface groups, which greatly simplify the simulation process. For instance, one can predict the locations of the hydroxyl groups by assuming Ti\(_3\)C\(_2\)Tx MXene is terminated with \(-\text{OH}\) groups only. As shown in Figure 4C, three possible configurations are predicted to exist according to the principle of energetically favorable termination orientations.\(^{47}\) In configuration X, \(-\text{OH}\) groups are positioned above the hallow sites between the neighboring C atoms. In configuration Y, \(-\text{OH}\) groups are located above the C atoms toward both sides of the Ti\(_3\)C\(_2\) layers. Configuration Z is defined as one side of the Ti\(_3\)C\(_2\) is in configuration X and the other side is in configuration Y. Other possible configurations are unstable and tend to transform into these three configurations.\(^{48}\) Moreover,

**FIGURE 4**  A, Structure of MAX phases and the corresponding MXenes. Reproduced with permission.\(^{18}\) Copyright 2018, Wiley-VCH. B, Schematic of MXene structures with more than one M atom. Reproduced with permission.\(^{25}\) Copyright 2015, American Chemical Society. C, Optimized atomic structures of (I) free-standing Ti\(_3\)C\(_2\) layer and (II-IV) its hydroxylated forms, Ti\(_3\)C\(_2\)(OH)\(_2\). The first row is the side view, the second row is the top view. Reproduced with permission.\(^{47}\) Copyright 2012, Elsevier
configuration X is found to have the lowest energy, suggesting the highest structure stability. In other words, the $-\text{OH}$ groups are more likely to arrange in configuration X in Ti$_3$C$_2$T$_x$ MXene.

In practice, MXene is terminated with mixed types of groups (OH, O, and F terminations), rendering the DFT calculations much more complex. Furthermore, water molecules are typically trapped among the layers, which for sure have a great influence on the stability, conductivity and capacitance in the energy storage device. In other words, understanding the surface groups (including distribution and arrangement of surface terminations) as well as the trapped water (and the water removal if needed) are useful for both theoretical studies and the resultant MXene properties. This is especially true for some applications that require MXenes with specific properties, which are typically obtained by engineering the surface functionalities and interlayer chemistries.

Unlike 2D graphene material, delaminated MXenes with single or few layer flakes are hydrophilic, and thus can form a stable dispersion in aqueous media without the addition of surfactant. In addition, due to the match of the Hansen solubility parameters, MXene nanosheets can be dispersed in a range of organic solvents, forming stable MXene organic solutions without the necessity of a binary solvent. We note this is a great advantage over graphene, allowing facile solution processing of MXene dispersions into any items or composites, and opening up great opportunities in thin-film coating, inkjet/extrusion printing, and many other applications. When dispersed in aqueous media, MXene nanosheets are vulnerable to oxidation by dissolved oxygen and water, highlighting the proper storage of the delaminated nanosheets solution. Zhang et al revealed that by isolating the solution from the dissolved oxygen through Ar-filling hematic bottles, which were placed in a low-temperature environment, the shelf-life of Ti$_3$C$_2$T$_x$ and Ti$_3$CT$_x$ aqueous solutions were greatly extended. Recently, Mochalin et al suggested that water is more pronounced in oxidizing MXene nanosheets; the solution’s stability was much improved when dispersing the nanosheets in isopropanol. Actually, by dispersing Ti$_3$C$_2$T$_x$ nanosheets in organic solvents like N-Methyl-2-Pyrrolidone (NMP), dimethyl sulfoxide (DMSO), dimethylformamide (DMF), the dispersions are stable over 12 months, showcasing the long-term stability.

According to DFT calculations, the electronic properties of Ti$_3$C$_2$T$_x$ layers are surface functionalities dependent. The theoretical calculations shows that bare Ti$_3$C$_2$ is a metallic conductor, which switches to a semiconductor as the surface is terminated by $-\text{OH}$ or $-\text{F}$ (bandgaps are 0.05 eV and 0.1 eV for Ti$_3$C$_2$(OH)$_2$ and Ti$_3$C$_2$F$_2$, respectively), as shown in Figure 5A.

![Figure 5](image-url)

**Figure 5** A. Calculated band structure of single-layer MXene with $-\text{OH}$ and $-\text{F}$ surface terminations and no termination (Ti$_3$C$_2$). Reproduced with permission. Copyright 2011, Wiley-VCH. B. Band structures near the Fermi level for (I) X-Ti$_3$C$_2$F$_2$, (II) Y-Ti$_3$C$_2$F$_2$, (III) Z-Ti$_3$C$_2$F$_2$, (IV) X-Ti$_3$C$_2$(OH)$_2$, (V) Y-Ti$_3$C$_2$(OH)$_2$, (VI) Z-Ti$_3$C$_2$(OH)$_2$. Reproduced with permission. Copyright 2012, American Chemical Society. C. Optical images of Ti$_3$C$_2$T$_x$ films on glass (I) and polyester (II) substrates, respectively (scale bars are 1 cm). (III) UV-vis spectra of Ti$_3$C$_2$T$_x$ films with different thicknesses. Reproduced with permission. Copyright 2016, Wiley-VCH.
MXenes are predicted to be semiconductors. Thus, the electronic properties of MXenes such as the bandgaps can be tuned by varying surface functional groups. The locations of surface functionalities also influence the band gap structures of MXenes. For instance, Ti$_3$C$_2$F$_2$ and Ti$_3$C$_2$(OH)$_2$ in the configuration Y (Figure 4C) are predicted to be metallic. In contrast, Ti$_3$C$_2$F$_2$ and Ti$_3$C$_2$(OH)$_2$ in configuration X and Z are shown to be semiconductors with narrow bandgaps (X-Ti$_3$C$_2$F$_2$:0.04 eV, Z-Ti$_3$C$_2$F$_2$:0.03 eV, X-Ti$_3$C$_2$(OH)$_2$:0.05 eV, Z-Ti$_3$C$_2$(OH)$_2$:0.07 eV) (Figure 5B). There are also some MXene phases with heavier transition metals such as chromium, molybdenum and tungsten that are predicted to be topological insulators. 24,56,57

The electrical conductivity of Ti$_3$C$_2$T$_x$ heavily depends on the preparation method. The sonicated, single-layer Ti$_3$C$_2$T$_x$ exhibits an electronic conductivity up to 6760 S cm$^{-1}$ while MILD-derived Ti$_3$C$_2$T$_x$ thin films possess values up to 10 000 S cm$^{-1}$.61 The elastic modulus of single-layer Ti$_3$C$_2$T$_x$ is calculated to be 10 000 S cm$^{-1}$ while MILD-derived Ti$_3$C$_2$T$_x$ thin films possess values up to 10 000 S cm$^{-1}$.61 The electronic conductivity of Ti$_3$C$_2$T$_x$ heavily depends on the preparation method. The sonicated, single-layer Ti$_3$C$_2$T$_x$ exhibits an electronic conductivity up to 6760 S cm$^{-1}$ while MILD-derived Ti$_3$C$_2$T$_x$ thin films possess values up to 10 000 S cm$^{-1}$.61

Thanks to the strong M-X bonds, MXenes are predicted to possess enhanced mechanical properties compared to their parental MAX phases.61 Moreover, MXenes are predicted to be stiffer and stronger than their MAX counterparts based on the DFT and molecular dynamics results. The elastic modulus of single Ti$_3$C$_2$T$_x$ sheet terminated with -OH is calculated to be 33,34,46,58-60

The conductivity of MXenes is affected by the preparation method. The sonicated, single-layer Ti$_3$C$_2$T$_x$ exhibits an electronic conductivity up to 6760 S cm$^{-1}$ while MILD-derived Ti$_3$C$_2$T$_x$ thin films possess values up to 10 000 S cm$^{-1}$.61 The elastic modulus of single-layer Ti$_3$C$_2$T$_x$ is calculated to be 10 000 S cm$^{-1}$ while MILD-derived Ti$_3$C$_2$T$_x$ thin films possess values up to 10 000 S cm$^{-1}$.61

The interaction behavior of MXenes and polysulfides is critical for the performance of Li-S batteries. Most theoretical studies on Ti-based MXenes mainly focus on the interaction behavior of Li$_2$S$_n$ and Ti$_3$CT$_x$ with various surface functional groups. DFT calculations indicate that the OH-terminated Ti$_3$C (Ti$_3$C (OH)$_2$) distort the long chain Li$_2$S$_n$. By contrast, the Li$_2$S$_n$ molecular configuration is maintained when it is absorbed on the surface of Ti$_3$CO$_2$ and Ti$_3$CF$_2$, indicating the strong interaction between MXenes and polysulfides.
that OH-terminated Ti$_2$C possesses stronger attractions for Li$_2$S$_n$ compared to that of Ti$_2$CO$_2$ and Ti$_2$CF$_2$. Actually, O and F functionalized Ti$_2$C MXenes show different suppressing mechanisms. O-functionalized surfaces tend to oxidize Li$_2$S$_n$ to neutral S which exhibits slight solubility. For the F-functionalized Ti$_2$C, it exhibits strong interaction with Li$_2$S$_n$. Figure 6C(I) shows the binding energy of Li$_2$S$_n$ on various functionalized Ti$_2$C MXenes. The differences of the binding energy could be originated from the Coulomb interactions between Li$_2$S$_n$ and MXenes (Figure 6CII). Bare MXenes possess strong Coulombic interactions and thus the induced Ti-S interactions are strong. When the Ti$_2$C surface is terminated with functional groups, Ti-S interactions will be reduced by the repulsive force from negatively charged groups (O/F to S). Li atoms also play a role in the Li$_2$S$_n$ binding. Although the interaction between Li and O/F could enhance the binding of Li$_2$S$_n$, these groups lead to a larger Ti-S distance and weaken the Li$_2$S$_n$ binding effect. This is why the binding energy of Li$_2$S$_n$ on bare MXenes is much stronger than that of functionalized MXenes. Since the O atoms in Ti$_2$C(OH)$_2$ are passivated with H atoms, the repulsive forces caused by negatively charged O atoms are reduced. The positively charged H atoms can enhance the attraction for S atoms. As a result, firm interactions between Li$_2$S$_n$ and Ti$_2$C(OH)$_2$ are obtained.

Some functional groups such as S and Cl can also be modified on the MXene surface to further suppress Li$_2$S$_n$ shuttling. S terminated Ti$_2$C is calculated to possess a higher efficiency to restrain the polysulfide shuttle as its binding energy is higher than that of O/F terminated MXenes.
Ti2C. S terminated Ti2C2Tx also exhibits the highest adsorption strength when compared with pristine Ti1.5C2Tx (T2 = OH, O, F) (Figure 6D).66,70

The theoretical analysis performed by Zhao et al indicates that Ti1.5C2(OH)2 becomes unstable after absorption of Li2Sn species; H atoms spontaneously migrate to S atoms of the Li2Sn while the remained O atoms interact with Li atoms, leading to the breakage of the Li2Sn species eventually.72 While the F-functionalized Ti2C showcases weak binding energy of Li2Sn, the Ti2CO2 and Ti1.5C2O2 MXenes exhibit similar binding energies for Li2Sn compared to that between Li2Sn and electrolyte. As a result, oxygen-terminated MXenes are more efficient in chemisorption of the polysulfides.67 Nevertheless, these DFT calculations were performed on the interactions between polysulfides and MXenes terminated with only one type of functional group, which is different from the real case where different types of functional groups may coexist on the MXenes, and may change the polysulfides suppression mechanism.71

The interaction behavior between Li2Sn and other MXenes has also been theoretically studied which may guide future rational selection of MXenes to act as sulfur hosts for Li-S batteries.65,72 Fan’s group investigated the Li2Sn anchoring behavior of five O-functionalized MXenes (M3C2O2, M = Cr, V, Nb, Hf and Zr) through DFT calculations.67 The study suggests that all the selected MXenes possess higher binding energies with Li2Sn than that with organic electrolytes (Figure 6EI), among which Cr3C2O2 MXene shows the strongest anchoring effect toward Li2Sn based on a lattice constant-dependent anchoring effect.67 The interactions with Li2Sn mainly originate from the Li-O covalent bonds (Figure 6EIII). When the lattice constant increases, the Li-O bond length extends and then structural distortion happens which weakens the interaction between Li2Sn and M3C2O2, reducing the binding energy.67

Some transition metal nitrides have already proved to be good sulfur host materials.73-76 Titanium nitride based MXenes are also potential conductive sulfur hosts with quite promising performance. Specifically, the anchoring mechanism of O- and F-functionalized Ti2N has been investigated.68 Based on the charge transfer analysis, chemical interactions are confirmed between Li2Sn and Ti2NO2, leading to a large adsorption energy (Figure 6F). For the Ti2NF2, the contribution to interactions is mainly van der Waals (vdW) interaction with less charge transfer from Li2Sn to Ti2F2O2.

### 3.2 Catalytic behavior of MXenes in Li-S batteries

Apart from the Li2Sn shuttling effect, the final discharged product Li2S with high decomposition energy would also compromise the electrochemical performances such as high overpotential and low rate capability. To this end, materials with high catalytic capability can effectively reduce the overpotential, promote the charge transfer kinetics process and improve the rate performance as a result. The 2D MXenes with various surface terminations exhibit unique catalytic capabilities and thus can be employed to address these issues.66,77,78 Surface-terminated Ti1.5C2Tx typically demonstrates strong interactions with Li2Sn while possessing a low Li2S decomposition barrier.66 Direct comparisons of Li2S decomposition barriers on the different surface-terminated MXenes are shown in Figure 7A. Unlike Ti3C2N2, Ti3C2F2 and Ti3C2Cl2, the Ti3C2S2 and Ti3C2O2 MXenes showcase much reduced Li2S decomposition barriers, which facilitate the decomposition of Li2S, shorten the Li2Sn accumulation time in the cathode and further suppress the Li2Sn dissolution. Ti3C2S2 can also maintain good catalytic capability even at high sulfur loading (Figure 7B).

Appropriate functional group vacancies could promote the interactions with Li2Sn species.70 For example, Ti3C2Cl2 exhibits poor adsorption capability and electrode reaction kinetic as the vdW interaction with Li2Sn species dominates the lithiation process. However, when Cl vacancies form on the Ti3C2Cl2 surface, the chemical interactions with Li2Sn could be increased, leading to improved Li2Sn adsorption capacity and further lowering down the decomposition energy of Li2S due to the presence of Cl vacancies (Figure 7C,D). Thus, surface modification is an efficient method to adjust the electrocatalysis behavior and to improve the electrode kinetics for boosting the electrochemical performances of Li-S batteries. Besides that, the total number of atomic layers of carbide-based MXenes also has an effect on catalytic ability.79

As a crucial aspect for Li2Sn nucleation and decomposition, fast Li+ diffusivity can assist the electrochemical process as well. Calculations on Ti1.5C2Tx demonstrate much lower Li+ diffusion barriers than that for graphene (Figure 7DIII-DVII).66 V-based MXenes with different surface terminations have also been studied, revealing that V2CS2 has a lower energy barrier for Li+ diffusion, facilitating the conversion of Li2Sn into low order Li2S (Figure 7E).78

Even when the MXene surface is covered by the polysulfides, the band gap of MXenes remain unchanged and MXenes can maintain their metallic properties to provide free electrons.65-67,69,70,73,78 We note that the good preservation of metallic host even after chemisorption of Li2Sn is beneficial for both the continuous redox reactions and the enhancement of active S utilization.

Based on the above discussions, MXenes possess substantial advantages in Li-S batteries due to their unique properties including surface chemistry, metallic conductivity and ultrathin nanosheet morphology, and so forth.
Understanding the Li$_2$S$_n$ anchoring and catalytic behaviors of MXenes are important for designing high-performance Li-S batteries, which will be discussed below.

4 | MXENE BASED LI-S BATTERIES

4.1 | Design of MXenes-based sulfur host in Li-S cathode

Introducing functional additives and constructing advanced structures for sulfur hosts are desirable strategies to entrap Li$_2$S$_n$ in the cathode and suppress the shuttle problem. Thanks to the strong interaction with polysulfides, MXenes with excellent electronic conductivity have been developed as highly effective sulfur cathode host materials, achieving improved cycling performance. Without optimization, low capacity decay rates (~0.05% per cycle) can be reached on the Ti$_3$C$_2$Tx MXene/S composites, which are comparative to various reported sulfur hosts such as graphene oxide and titanium oxide, and so forth. Beside the utilization as sulfur cathode, MXenes can also be used to fabricate Ti$_3$C$_2$Tx/Li$_2$S cathodes to further improve the Li$_2$S$_n$ trapping ability.

Delaminated MXene sheets are easily restacked due to the vdW interactions which may hinder the chemical interaction with polysulfides. To improve the MXene nanosheet utilization, one desirable strategy is to develop MXene based hybrids through introducing spacers among...
the MXene layers. Nazar’s group reported a porous and conductive Ti$_3$C$_2$T$_x$/carbon nanotube (CNT) structure as sulfur host. The CNTs dispersed among the MXene sheets effectively suppress the nanosheets restacking, and thus achieve a high surface area (MXene/CNT: 350 m$^2$ g$^{-1}$, exceeding the sum surface area of MXene and CNT) which is beneficial for both physically confinement of Li$_2$S$_n$ and enhanced utilization of chemisorptive MXene polar sites. Interconnecting CNTs in the MXene can maintain high electrical conductivity and facilitate the electron transport. Carbon fibers (CF) and reduced graphene oxide (rGO) are typically used to hybridize with MXenes so as to alleviate the MXene nanosheet restacking phenomenon (Figure 8A). The alternative strategy is to construct three-dimensional (3D) MXene architectures by introducing Ti$_3$C$_2$T$_x$ sheets into porous skeletons as polysulfide reservoir to improve the utilization of the Ti$_3$C$_2$T$_x$ sheets. For example, the Ti$_3$C$_2$T$_x$/mesoporous carbon matrix exhibits a higher surface area of 1531.9 m$^2$ g$^{-1}$ and pore volume of 0.577 cm$^3$ g$^{-1}$ than those of restacked Ti$_3$C$_2$T$_x$/mesoporous carbon mixtures, suggesting the important role of the 3D matrix. Besides the mesoporous carbon, MXene/graphene aerogel also provides large spaces for encapsulating sulfur and accommodating the volumetric expansion of the cathode (Figure 8B,C).

Utilizing conductive carbon materials as additives can effectively improve the electrochemical performances of MXene/S cathode. However, the weak affinity among different host materials increases the interfacial transfer resistance and slows down the reaction kinetics of sulfur species. To improve the affinity to sulfur, a crumpled nitrogen-doped Ti$_3$C$_2$T$_x$ (N-Ti$_3$C$_2$T$_x$) nanosheet with well-defined porous structure was developed by Wang’s group, as shown in Figure 9A(I). This optimized MXene structure possesses a 10 times enhanced surface area (385.4 m$^2$ g$^{-1}$) and large pore volume (0.342 cm$^3$ g$^{-1}$) compared with those of the mechanically mixed Ti$_3$C$_2$T$_x$ (surface area: 30 m$^2$ g$^{-1}$, pore volume: 0.0321 cm$^3$ g$^{-1}$, Figure 9A[II]). Such nitrogen-doped MXenes also showcase a greater capability to adsorb polysulfides than that of pure MXenes, demonstrating an improving reversible capacity of 950 mAh g$^{-1}$ after 200 cycles at 0.2C (Figure 9A[III]). Beyond nitrogen doping to promote the surface polarity, the redox reactivity of sodium polysulfides can also be enhanced by incorporating sulfur surface groups on MXenes to boost the performance of Na-S batteries. In another case, Ti$_3$C$_2$T$_x$ nanodots as spacer were integrated among the Ti$_3$C$_2$T$_x$ nanosheets (TCD-TCS), as shown in Figure 9B(I). Such a nanostructure exposes more surface terminations and provides large amounts of active sites to trap the Li$_2$S$_n$, thus boosting the overall performances of the electrode (Figure 9BII-IV).

Materials with polar sites such as TiO$_2$, polydopamine (PDA), MnO$_2$, and MoS$_2$ have also been composited with MXenes as sulfur hosts to increase the active polysulfide entrapping sites and to enhance the Li$_2$S$_n$ immobilization.

**FIGURE 8** Various designs to prevent MXenes from restacking. A, Schematic illustration of Ti$_3$C$_2$T$_x$/rGO fabrication. Reproduced with permission. Copyright 2017, Wiley-VCH. B, Synthesis procedure of the Ti$_3$C$_2$T$_x$/mesoporous carbon (Meso-C) composites. Reproduced with permission. Copyright 2016, Wiley-VCH. C, Preparation process of the Ti$_3$C$_2$T$_x$/rGO aerogel electrodes. Reproduced with permission. Copyright 2019, The Royal Society of Chemistry
capability, respectively. Figure 10 summarizes the detailed materials synthesis strategies, including oxide loading, freeze-drying, polymer coating, pumping, solvothermal and hydrothermal, and so forth. The as-obtained Ti$_3$C$_2$Tx based heterostructures well preserve the 2D layered geometry and alleviate the nanosheet restacking, greatly opening up more polysulfide entrapping sites.

For instance, MXene decorated with TiO$_2$ quantum dots (QDs) as sulfur host showcases quite promising performance for achieving fast and stable Li-S batteries. Compared with a MXene/S cathode which displayed 308 mAh g$^{-1}$ at 1C (1C = 1675 mA g$^{-1}$) after 500 cycles (Figure 11A), due to the stronger adsorption ability of Li$_2$Sn species in the latter. Similarly, another polar hybrid sulfur host was achieved by confining conductive MXenes into 1T-2H MoS$_2$-nitrogen-doped carbon (Ti$_3$C$_2$Tx/1T-2H MoS$_2$-C) composites, demonstrating a higher initial capacity of 1194.7 mAh g$^{-1}$ at 0.1C than that of MXene/S electrode (845.1mAh g$^{-1}$) (Figure 11B). After cycling, the black surface of Ti$_3$C$_2$Tx/1T-2H MoS$_2$-C cathode without obvious sulfur spots, coupled with the flat, shining Li metal surface, suggests that the Li$_2$Sn shuffling has been effectively suppressed and the smooth deposition of Li during upon repeated charge-discharge processes.

While titanium carbides have been widely studied as sulfur host, other types of MXenes, with different
electronic conductivity, surface chemistry and other properties, certainly deserve to be explored for the Li-S battery applications. For instance, Mo$_2$CT$_x$ MXene was confirmed with good capability in immobilizing polysulfides due to the Lewis acid-base interaction from the Mo atoms with Li$_2$Sn.\textsuperscript{100} By interweaving with CNTs, a highly conductive Mo$_2$CT$_x$ MXene-CNT hybrid was developed as sulfur host, as shown in Figure 12A. The Mo$_2$CT$_x$/CNTs electrode delivered excellent electrochemical performances in terms of high capacity, good rate capability and high initial reversible capacity at various sulfur loading (1314 mAh g$^{-1}$ at 1.8 mg cm$^{-2}$ sulfur loading, 959 mAh g$^{-1}$ at 5.6 mg cm$^{-2}$ sulfur loading) (Figure 12A).\textsuperscript{100} Composites based on hybridizing Mo$_2$C with CNF (Mo$_2$C/CNFs, Figure 12B) and a porous carbon matrix (Mo$_2$C/C, Figure 12C), respectively were also reported as sulfur hosts to facilitate electron transport and lithium ion diffusion, showcasing good Li$_2$Sn immobilization capability.\textsuperscript{101-103} We note that metal carbides play important roles in enhancing the polysulfide anchoring, improving the electrocatalytic kinetics and accelerating the polysulfide conversion into lower-order Li$_2$S (Figure 12D). Similarly, tungsten carbide (W$_2$C) was reported as an efficient sulfur host with stable cycling for Li-S batteries, which could be ascribed to the enhanced adsorption and catalytic sites on W$_2$C. For example, decorating W$_2$C nanoparticles on the

**FIGURE 10**  A, Schematic illustration of the Ti$_3$C$_2$T$_x$/TiO$_2$/S composite synthesis. Reproduced with permission.\textsuperscript{94} Copyright 2019, Elsevier. B, Schematic illustration shows the synthesis processes of Ti$_3$C$_2$T$_x$/MnO$_2$/S composites. Reproduced with permission.\textsuperscript{95} Copyright 2019, American Chemical Society. C, Schematic illustration of Ti$_3$C$_2$T$_x$/PDA/S fabrication. Reproduced with permission.\textsuperscript{96} Copyright 2019, Elsevier. D, Schematic illustration of the synthesis process of TiO$_2$/Ti$_2$C/S composites. Reproduced with permission.\textsuperscript{97} Copyright 2019, Elsevier
CNF (W₂C NPs/CNFs) and loading W₂C nanoclusters on the nitrogen-phosphorous co-doped carbon matrix (W₂C/N/P-rGO) (Figure 12EI) resulted in composites with enhanced polysulfides interaction and improved electrochemical kinetics. The W₂C/N/P-rGO composites delivered high reversible capacities under different sulfur loadings (Figure 12EII,III). Another important aspect of MXenes in Li-S battery is the employment as separator. As we know, Li₂Sn diffusion not only causes active mass loss, but also results in unfavorable reactions with the Li anode, causing significant polarization. In addition to develop advanced sulfur hosts, adding an Li₂Sn absorptive interlayer or fabricating functional separators can further improve the electrochemical performances of Li-S batteries. For example, when inserting a CNT freestanding interlayer between MXene/S cathode and separator, the separator almost remained its original color after cycling and achieved better electrochemical performances compared to the cell without CNT interlayer (the color of the separator changed to a light yellowish color after cycling), indicating the inserted CNT membrane efficiently block the migration of Li₂Sn. Inspired by this design, Wang et al modified the separator by coating a MXene thin film onto the battery

4.2 | MXene as separator in Li-S battery

Another important aspect of MXenes in Li-S battery is the employment as separator. As we know, Li₂Sn diffusion not only causes active mass loss, but also results in unfavorable reactions with the Li anode, causing significant polarization. In addition to develop advanced sulfur hosts, adding an Li₂Sn absorptive interlayer or fabricating functional separators can further improve the electrochemical performances of Li-S batteries. For example, when inserting a CNT freestanding interlayer between MXene/S cathode and separator, the separator almost remained its original color after cycling and achieved better electrochemical performances compared to the cell without CNT interlayer (the color of the separator changed to a light yellowish color after cycling), indicating the inserted CNT membrane efficiently block the migration of Li₂Sn.

Inspired by this design, Wang et al modified the separator by coating a MXene thin film onto the battery.
Celgard separator, in which the coated conductive MXene film acts as a second current collector to reduce the electron transfer resistance as well as suppresses the polysulfide shuttling effects,\textsuperscript{110} as shown in Figure 13A. Consequently, Li-S batteries with a Ti$_3$C$_2$Tx-modified separator exhibit better cycling retention and reversibility than that of the pristine battery.\textsuperscript{110} Based on the preliminary research on the MXene for modifying separators, extensive studies have been devoted to optimizing the structures such as Ti$_3$C$_2$Tx/GF,\textsuperscript{111} Ti$_3$C$_2$Tx/eggshell membrane (ESM),\textsuperscript{112} Ti$_3$C$_2$Tx/CNT,\textsuperscript{113} N-Ti$_3$C$_2$Tx/C\textsuperscript{114} and Ti$_3$C$_2$Tx/Nafion\textsuperscript{115} (Figure 13B-E). MXene-modified separators also facilitate good areal capacity under high sulfur loading. For a Ti$_3$C$_2$Tx/Nafion modified polypropylene (PP) separator, the Li-S cell achieved a reversible areal capacity of 5 mAh cm$^{-2}$ with sulfur loading of 6.0 mg cm$^{-2}$.\textsuperscript{115} When loading an impressively high amount of sulfur (10 mg cm$^{-2}$), very high areal capacity of 6.3 mAh cm$^{-2}$ was achieved with the N-Ti$_3$C$_2$Tx/C coated PP separator.\textsuperscript{114}

It should be noted that the coated MXene-based composites usually have a dense laminar structure which may hinder the effective infiltration of electrolyte. Meanwhile, insulating Li$_2$S/Li$_2$S$_2$ products keep accumulating on the separator, leading to increased interfacial charge transfer resistance and sluggish ion transport kinetics. As a result, serious polarization and capacity decay especially under high sulfur loading or at high rate may occur. In addition, the MXene nanosheets stacking behavior (ordered vs random) is also important for
achieving high Li-S performances. In any case, the modified layer partially suppresses the diffusion of Li$_2$Sn species and inhibits Li$^+$ mobility to some extent, highlighting the importance of optimization on the MXene membrane thickness.

4.3 Comprehensive Li-S cell design based on MXenes

To further improve the Li-S battery performance, some strategies are proposed by comprehensively designing MXene-based cathodes and separators. For instance, Wu et al reported the employment of Ti$_3$C$_2$T$_x$ MXene for hosting sulfur and modifying the separator. By using 3D alkalized Ti$_3$C$_2$T$_x$ MXene nanoribbon as sulfur host, as well as a 2D Ti$_3$C$_2$T$_x$ nanosheet coated on the separator, a high S loading coupled with high reversible capacity (1062 mAh g$^{-1}$ at 0.2C) and energy density (833 Wh kg$^{-1}$) were achieved, as shown in Figure 14A. Very recently, an antifouling separator of self-assembled Ti$_3$C$_2$T$_x$/CNT-polyethylenimine (Ti$_3$C$_2$T$_x$/CNT-P) composite was reported (Figure 14BI). The nanohybrid based separator possesses well-developed 3D conductive channels and good affinity to polysulfides. These advantages from the hybrid membrane allow rapid electrolyte transport as well as fully utilization of active species. As a result of the comprehensive cell design, the pouch cell demonstrated excellent rate performance (1110, 1035 and 950 mAh g$^{-1}$ at 0.5C, 1C and 2.5C, respectively) and stable cycling performance under high sulfur loading of 5.8 mg cm$^{-2}$ (Figure 14BII,BIII).

Combining the advantages of Li$_2$Sn immobilization and high electrocatalytic properties, a multifunctional Ti$_3$C$_2$T$_x$/TiO$_2$ heterostructure was prepared by a controlled oxidation process of MXenes. The in-situ formation of Ti$_3$C$_2$T$_x$/TiO$_2$ heterostructure with stronger Li$_2$Sn chemisorption capability ensures smooth Li$_2$Sn diffusion to the MXene and then accelerate the conversion to low-order Li$_2$S$_{1-2}$ (Figure 14CI). The Ti$_3$C$_2$T$_x$/TiO$_2$ could also act as interlayer for the Li-S pouch cell with stable cycling, ultralow capacity decay rate (0.028% per cycle over 1000 cycles at 2C) and excellent capacity retention (93% after 200 cycles) even at a high sulfur loading of 5.1 mg cm$^{-2}$ (Figure 14CII).

Another important aspect for achieving high-performance Li-S batteries is to fabricate electrodes with a high sulfur loading amount. Therefore, utilizing a highly conductive host is quite necessary so as to maintain good electron transport paths after loading a large amount of insulating sulfur. Constructing 3D microporous channels to form MXene foam, as well as increasing...
interlayer spacing by pillaring the nanosheets in order to increase surface area, are promising routes for achieving high sulfur loading electrodes. For example, the self-supported Ti₃C₂Tx foam was able to uniformly accommodate a large amount of sulfur due to the well-defined porous structure. Consequently, the cell still maintained 689.7 mAh g⁻¹ after 1000 cycles with sulfur loading of 5.1 mg cm⁻² (Figure 15A). Recently, Wang et al designed a flower-like porous Ti₃C₂Tx nanomesh, in which well-aligned conductive Ti₃C₂Tx nanosheets provide abundant active sites to entrap polysulfides, allowing rapid electron/ion transport and electrolyte penetration for fast redox reactions (Figure 15B). Based on this structure, the sulfur mass loading was improved to 10.5 mg cm⁻², resulting in high areal and volumetric capacities (10.04 mAh cm⁻² and 2009 mAh cm⁻³) (Figure 15C). The abovementioned Ti₃C₂Tx nanodots in nanosheets electrode configuration (TCD-TCS) demonstrated the highest sulfur loading (13.8 mg cm⁻²) among the reports, leading to an areal capacity of 13.7 mAh cm⁻² that is three times higher than that of commercialized Li-ion batteries (~4 mAh cm⁻², Figure 15D). Table 1 summarizes the areal capacities of MXene-based Li-S batteries with high sulfur loadings.

4.4 Novel design for MXene-based Li-S battery

To match the trends of the fast-growing portable and wearable devices, power sources should also be flexible and robust enough. This requires the sulfur electrodes to be highly resilient while exhibiting excellent capacities upon bending or twisting. To address these challenging issues, a general strategy is to embed sulfur into a conductive matrix with impressive mechanical properties. As detailed previously, 2D Ti₃C₂Tx MXenes possess metallic conductivity and the nanosheets showcase an ultrahigh
**FIGURE 15** A, Schematic illustration of Ti$_3$C$_2$Tx foam/S in the charge/discharge process. Reproduced with permission.\(^{123}\) Copyright 2018, The Royal Society of Chemistry. B, Schematic illustration of synthesizing flower-like Ti$_3$C$_2$Tx and the formation mechanism of the nanomeshes in the Ti$_3$C$_2$Tx nanosheet. C, Areal and volumetric capacities at 1/30C for the flower-like Ti$_3$C$_2$Tx electrode under various sulfur loadings. Reproduced with permission.\(^{124}\) Copyright 2019, American Chemical Society. D, (I) Schematic of Ti$_3$C$_2$Tx TCD-TCS/S composites, (II) cycling performance of Ti$_3$C$_2$Tx TCD-TCS electrodes under sulfur loading of 13.8 mg cm\(^{-2}\) at 0.05C. Reproduced with permission.\(^{93}\) Copyright 2019, American Chemical Society

**TABLE 1** Summary of areal capacity and sulfur loading of reported MXene based Li-S batteries

<table>
<thead>
<tr>
<th>Materials</th>
<th>Application</th>
<th>Sulfur loading (mg cm(^{-2}))</th>
<th>Areal capacity (mAh cm(^{-2}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$_2$CT$_x$/C</td>
<td>Cathode host</td>
<td>4.2</td>
<td>1.1/1C</td>
<td>102</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/CF(^a)</td>
<td>Cathode host</td>
<td>5</td>
<td>3.2/1 mA/cm(^{-2})</td>
<td>86</td>
</tr>
<tr>
<td>Crumpled N-Ti$_3$C$_2$Tx</td>
<td>Cathode host</td>
<td>5.1</td>
<td>4.2/0.2C</td>
<td>91</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/CNT(^b)</td>
<td>Cathode host</td>
<td>5.5</td>
<td>5/0.05C</td>
<td>23</td>
</tr>
<tr>
<td>Mo$_2$CT$_x$/CNT</td>
<td>Cathode host</td>
<td>5.6</td>
<td>5.3/0.1C</td>
<td>100</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/CNT-P(^c)</td>
<td>Separator</td>
<td>5.8</td>
<td>7.1/0.25C</td>
<td>118</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/Nafion</td>
<td>Separator</td>
<td>6</td>
<td>5/0.2C</td>
<td>114</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/rGO aerogel</td>
<td>Cathode host</td>
<td>6</td>
<td>5.27/0.1C</td>
<td>89</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/graphene/Li$_2$S</td>
<td>Cathode host</td>
<td>9</td>
<td>5.04/0.2C</td>
<td>90</td>
</tr>
<tr>
<td>N-Ti$_3$C$_2$Tx/C</td>
<td>Separator</td>
<td>10</td>
<td>6.3/0.1C</td>
<td>115</td>
</tr>
<tr>
<td>Flower-like Ti$_3$C$_2$Tx</td>
<td>Cathode host</td>
<td>10.5</td>
<td>10.04/0.03C</td>
<td>124</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx (TCD-TCS)(^d)</td>
<td>Cathode host</td>
<td>13.8</td>
<td>13.7/0.05C</td>
<td>93</td>
</tr>
</tbody>
</table>

\(^{a}\)Carbon fiber (CF).  
\(^{b}\)Carbon nanotube (CNT).  
\(^{c}\)Polyethyleneimine (P).  
\(^{d}\)Ti$_3$C$_2$Tx nanodots/nanosheets (TCD-TCS).
tensile strength of 300 MGa. Thus, delaminated Ti$_3$C$_2$Tx MXene nanosheets can be used as conductive binder and backbone for flexible sulfur cathode. For example, a free-standing Ti$_3$C$_2$Tx electrode with ultramicroporous channels was employed to encapsulate small sulfur molecules (Ti$_3$C$_2$Tx-UMC/S$_2$), achieving both excellent flexibility and high charge-storage performances. The MXene/1T-2H MoS$_2$-C electrode also showcases excellent mechanical properties, which can withstand repeated bending without compromising the electrochemical performances, demonstrating its potential applications in the flexible Li-S pouch cell.

To further improve the electrical, mechanical and electrochemical performances of MXene-S electrodes, Zhang et al.
et al reported an aqueous Ti$_3$C$_2$Tx MXene-S composite ink, by which electrodes with high S content (70%) were quickly fabricated through a commercialized slurry casting technique. Thanks to the high concentration and viscosity from the composite ink, the as-formed Ti$_3$C$_2$Tx-S freestanding electrodes were highly conductive and flexible that was achieved in the absence of additional conductive agents and polymeric binders (Figure 16AI-III). The architecture based on the highly conductive network ensures intimate contact between sulfur species and Ti$_3$S$_n$ species. Combined with Lewis acid-base interaction between Ti atoms and Li$_2$Sn species, the Li-S batteries exhibited excellent electrochemical performances including high capacity of 1244 to 1350 mA h g$^{-1}$ and impressive cycling stability (0.035-0.048% capacity loss per cycle), showing great promise for applications in wearable device (Figure 16AIV-VI). Very recently, Zhang et al further extended the applications of the viscous MXene aqueous inks, including constructing high capacity MXene-silicon anodes and additive-free printing of micro-supercapacitor.

Furthermore, Zhang et al prepared MXene/S conductive paper as electrodes by filtration the viscous MXene ink, followed by S impregnation, as demonstrated in Figure 16Bl. Such robust electrodes showcased excellent long-term cycling performance with a capacity decay rate of 0.014% per cycle, which has greatly surpassed all other MXene-S electrodes in terms of cycling stability, as shown in Table 2. A prototype full cell based on MXene/S paper and lithium foil is demonstrated in Figure 16BII-BIV, implying the promising applications in next-generation wearable, portable electronics.

5 SUMMARY AND OUTLOOK

In this work, we summarize the applications of MXenes for Li-S batteries. Due to their exotic properties, such as abundant surface terminated groups, excellent electronic conductivity and mechanical strength, and so on, MXenes have been widely used in various fields. Table 2 summarizes the electrochemical performances of MXene-based Li-S batteries. The table includes the materials used, the specific capacity, cycle life, and capacity decay rate. Further studies are needed to optimize these systems for practical applications.

### Table 2

<table>
<thead>
<tr>
<th>Materials</th>
<th>Application</th>
<th>Sulfur content/sulfur loading</th>
<th>Specific capacity (mAh g$^{-1}$)</th>
<th>Cycle life (cycles)</th>
<th>Capacity decay rate (% per cycle)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$CT$_x$</td>
<td>Cathode host</td>
<td>70 wt%</td>
<td>1090/0.5C</td>
<td>650/0.5C</td>
<td>0.05</td>
<td>22</td>
</tr>
<tr>
<td>Ti$_2$CT$_x$/CNT</td>
<td>Cathode host</td>
<td>83 wt%/1.5 mg cm$^{-2}$</td>
<td>1240/0.05C</td>
<td>1263/0.05C</td>
<td>0.043</td>
<td>23</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx</td>
<td>Cathode host</td>
<td>57.6 wt%</td>
<td>1291/200 mA g$^{-1}$</td>
<td>100/200 mA g$^{-1}$</td>
<td>0.25</td>
<td>80</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/Li$_2$S</td>
<td>Cathode host</td>
<td>0.8 mg cm$^{-2}$</td>
<td>630/0.2C</td>
<td>100/0.2C</td>
<td>0.2857</td>
<td>85</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/CF</td>
<td>Cathode host</td>
<td>1.2 mg cm$^{-2}$</td>
<td>1380/0.1C</td>
<td>1000/1C</td>
<td>0.044</td>
<td>86</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/rGO</td>
<td>Cathode host</td>
<td>70.4 wt%</td>
<td>1144.2/0.5C</td>
<td>300/0.5C</td>
<td>0.0774</td>
<td>87</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/Meso-C</td>
<td>Cathode host</td>
<td>72.88 wt%/2.0 mg cm$^{-2}$</td>
<td>1225.8/0.5C</td>
<td>300/0.5C</td>
<td>0.142</td>
<td>88</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/rGO aerogel</td>
<td>Cathode host</td>
<td>45 wt%/1.57 mg cm$^{-2}$</td>
<td>1270/0.1C</td>
<td>500/1C</td>
<td>0.07</td>
<td>89</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/graphene/Li$_2$S</td>
<td>Cathode host</td>
<td>62 wt%/3 mg cm$^{-2}$</td>
<td>710/0.2C</td>
<td>100/0.2C</td>
<td>0.133</td>
<td>90</td>
</tr>
<tr>
<td>Crumpled N-Ti$_3$C$_2$Tx</td>
<td>Cathode host</td>
<td>73.85 wt%/1.5 mg cm$^{-2}$</td>
<td>1609/0.05C</td>
<td>1000/2C</td>
<td>0.026</td>
<td>91</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx (TCD-TCS)</td>
<td>Cathode host</td>
<td>67.6 wt%/1.8 mg cm$^{-2}$</td>
<td>1609/0.05C</td>
<td>400/2C</td>
<td>0.057</td>
<td>93</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/TiO$_2$</td>
<td>Cathode host</td>
<td>60 wt%</td>
<td>1417/1C</td>
<td>1000/1C</td>
<td>0.053</td>
<td>94</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/MnO$_2$</td>
<td>Cathode host</td>
<td>70 wt%/1.2 mg cm$^{-2}$</td>
<td>1140/0.05C</td>
<td>500/1C</td>
<td>0.06</td>
<td>95</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/PDA$^b$</td>
<td>Cathode host</td>
<td>78.3 wt%/5 mg cm$^{-2}$</td>
<td>1001/0.2C</td>
<td>1000/2C</td>
<td>0.035</td>
<td>96</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/TiO$_2$</td>
<td>Cathode host</td>
<td>78.4 wt%/1.8-2.0 mg cm$^{-2}$</td>
<td>1408.6/0.1C</td>
<td>200/2C</td>
<td>0.2036</td>
<td>97</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx/TiO$_2$ QDsc</td>
<td>Cathode host</td>
<td>80 wt%/1.5 mg cm$^{-2}$</td>
<td>1158/0.2C</td>
<td>500/2C</td>
<td>0.04</td>
<td>98</td>
</tr>
</tbody>
</table>

(Continues)
<table>
<thead>
<tr>
<th>Materials</th>
<th>Application</th>
<th>Sulfur content/sulfur loading</th>
<th>Specific capacity (mAh g(^{-1}))</th>
<th>Cycle life (cycles)</th>
<th>Capacity decay rate (% per cycle)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx/1T-2H MoS(_2)-C</td>
<td>Cathode host</td>
<td>79.6 wt%/1 mg cm(^{-2})</td>
<td>1194.7/0.1C</td>
<td>300/0.5C</td>
<td>0.07</td>
<td>99</td>
</tr>
<tr>
<td>Mo(_2)C(_2)Tx/CNT</td>
<td>Cathode host</td>
<td>87.1 wt%/0.8 mg cm(^{-2})</td>
<td>1438/0.1C</td>
<td>1438/0.1C</td>
<td>0.1</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5 mg cm(^{-2})</td>
<td>1414/0.1C</td>
<td>250/0.1C</td>
<td>0.1</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.5 mg cm(^{-2})</td>
<td>1068/0.1C</td>
<td>250/0.1C</td>
<td>0.1</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.6 mg cm(^{-2})</td>
<td>959/0.1C</td>
<td>250/0.1C</td>
<td>0.1</td>
<td>100</td>
</tr>
<tr>
<td>Mo(_2)C/CNFs</td>
<td>Cathode host</td>
<td>1.5 mg cm(^{-2})</td>
<td>1017/0.1C</td>
<td>1017/0.1C</td>
<td>0.4916</td>
<td>101</td>
</tr>
<tr>
<td>Mo(_2)C NPs/CNFs</td>
<td>Cathode host</td>
<td>2.5 mg cm(^{-2})</td>
<td>1085/0.2C</td>
<td>1085/0.2C</td>
<td>0.156</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>72.15 wt%/1.1 mg cm(^{-2})</td>
<td>1050/1C</td>
<td>1050/1C</td>
<td>0.0457</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.1 mg cm(^{-2})</td>
<td>990/0.5C</td>
<td>1000/0.5C</td>
<td>0.156</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.2 mg cm(^{-2})</td>
<td>914/0.5C</td>
<td>1000/0.5C</td>
<td>0.249</td>
<td>103</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.2 mg cm(^{-2})</td>
<td>807/0.5</td>
<td>1000/0.5C</td>
<td>0.228</td>
<td>103</td>
</tr>
<tr>
<td>W(_2)C/N/P-rGO</td>
<td>Cathode host</td>
<td>63 wt%/1.5 mg cm(^{-2})</td>
<td>914/1C</td>
<td>400/1C</td>
<td>0.0777</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.1 mg cm(^{-2})</td>
<td>888/0.5C</td>
<td>1000/0.5C</td>
<td>0.0653</td>
<td>104</td>
</tr>
<tr>
<td>W(_2)C NPs/CNFs</td>
<td>Cathode host</td>
<td>2.5 mg cm(^{-2})</td>
<td>1200/0.2C</td>
<td>1200/0.2C</td>
<td>0.06</td>
<td>102</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx</td>
<td>Separator</td>
<td>50 wt%//1.0-1.2 mg cm(^{-2})</td>
<td>1458/0.1A g</td>
<td>1500/0.8 A g(^{-1})</td>
<td>0.04</td>
<td>109</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx</td>
<td>Separator</td>
<td>68 wt%/1.2 mg cm(^{-2})</td>
<td>1046.9/0.2C</td>
<td>500/0.5C</td>
<td>0.062</td>
<td>110</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx/GF</td>
<td>Separator</td>
<td>70 wt%/1.9 mg cm(^{-2})</td>
<td>1462/0.1 A g(^{-1})</td>
<td>100/0.5 A g(^{-1})</td>
<td>0.22</td>
<td>111</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx/ESM(_d)</td>
<td>Separator</td>
<td>67 wt%/2.07 mg cm(^{-2})</td>
<td>1003/0.5C</td>
<td>250/0.5C</td>
<td>0.104</td>
<td>112</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx/CNT</td>
<td>Separator</td>
<td>70 wt%/0.8 mg cm(^{-2})</td>
<td>1415/0.1C</td>
<td>600/1C</td>
<td>0.06</td>
<td>113</td>
</tr>
<tr>
<td>N-Ti(_3)C(_2)Tx/C</td>
<td>Separator</td>
<td>79 wt%/3.4 mg cm(^{-2})</td>
<td>1332/0.1C</td>
<td>500/0.5C</td>
<td>0.07</td>
<td>114</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx/Nafion</td>
<td>Separator</td>
<td>74.1 wt%/2 mg cm(^{-2})</td>
<td>1234/0.2C</td>
<td>1000/1C</td>
<td>0.03</td>
<td>115</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx/MNR(_e)</td>
<td>Cathode host</td>
<td>68 wt%/0.7-1 mg cm(^{-2})</td>
<td>1062/0.2C</td>
<td>200/0.5C</td>
<td>0.2615</td>
<td>117</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx/CNT-P</td>
<td>Cathode host</td>
<td>70.2 wt%/2.6 mg cm(^{-2})</td>
<td>1110/0.5C</td>
<td>500/1C</td>
<td>0.021</td>
<td>118</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx/TiO(_2)</td>
<td>Separator</td>
<td>75 wt%/1.2 mg cm(^{-2})</td>
<td>800/2C</td>
<td>1000/2C</td>
<td>0.028</td>
<td>119</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx/TiO(_2) foam</td>
<td>Cathode host</td>
<td>71.1 wt%/1.5 mg cm(^{-2})</td>
<td>1226.4/0.2C</td>
<td>1000/1C</td>
<td>0.05</td>
<td>123</td>
</tr>
<tr>
<td>Flower-like Ti(_3)C(_2)Tx</td>
<td>Cathode host</td>
<td>61.5 wt%/4.2 mg cm(^{-2})</td>
<td>1178/0.033C</td>
<td>1178/0.033C</td>
<td>0.366</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.8 mg cm(^{-2})</td>
<td>1120/0.033C</td>
<td>1120/0.033C</td>
<td>0.375</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.5 mg cm(^{-2})</td>
<td>957/0.033C</td>
<td>1120/0.033C</td>
<td>0.294</td>
<td>124</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx/S(_2)-UMC(_f)</td>
<td>Cathode host</td>
<td>37.2 wt%</td>
<td>1029.7/0.1C</td>
<td>200/0.1C</td>
<td>0.0405</td>
<td>127</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx/S film</td>
<td>Cathode host</td>
<td>70 wt%</td>
<td>1244/0.1C</td>
<td>800/0.2C</td>
<td>0.048</td>
<td>128</td>
</tr>
<tr>
<td>Ti(_3)C(_2)Tx/S paper</td>
<td>Cathode host</td>
<td>30 wt%</td>
<td>1383/0.1C</td>
<td>150/1C</td>
<td>0.014</td>
<td>130</td>
</tr>
</tbody>
</table>

\(^a\)Mesoporous carbon (Meso-C).
\(^b\)Polydopamine (PDA).
\(^c\)Quantum dots (QDs).
\(^d\)Ti\(_3\)C\(_2\)Tx nanodots/nanosheets (TCD-TCS).
\(^e\)MXene nanoribbon (MNR).
\(^f\)Sulfur molecules (UMC).
forth, the laminated MXenes possess many unique advantages over other 2D materials and are quite promising for constructing high-performance electrodes. Specifically, (a) the unique layered structure endows MXene nanosheet with sufficient contact area for sulfur/sulfides, and provides good mechanical strength to withstand the stress induced by large volume expansion of sulfur; (b) the metallic conductivity facilitates the electron transport kinetics across the electrode/electrolyte interface, alleviates electrode polarizations and facilitates high rate responses even at a high sulfur loading; (c) MXenes can entrap the soluble Li$_2$S$_n$ though a strong Ti-S interaction to suppress the shuttling effect. Meanwhile, MXene surface functional groups also have a strong chemisorption to Li$_2$S, which efficiently reduces the active material loss and maintain high capacities after long-term cycling; (d) MXenes with specific surface groups and configurations show a low Li$_2$S decomposition energy barrier and fast Li$^+$ diffusivity, leading to good catalytic performance and facilitating the electrochemical redox reactions.

Based on these merits, MXenes have been devoted as both sulfur hosts and modified separators. The electrochemical performances of MXene-based Li-S batteries can be improved mainly through the materials and cell design. For instance, increasing the active interaction sites to strength Li$_2$S$_n$ immobilization, introducing spacers to suppress the nanosheet restacking and constructing 3D frameworks to enhance sulfur loading, and so forth. We believe the electrochemical performance of MXene-based electrodes/devices can be further improved through the following categories.

First, the most common way to synthesize MXenes is by etching of the MAX phase. As a result, functional surface groups are inevitably terminated on the MXenes. According to the theoretical analysis, MXene surface groups play an important role in confining Li$_2$S$_n$. The interaction mode of Ti-S is influenced by the functional groups like $-\text{O}$, $-\text{OH}$, $-\text{F}$, $-\text{S}$, and so forth. On the one hand, reducing the amount of these terminations is beneficial to form strong Ti–S bonds. On the other side, Li$_2$S$_n$ species are prefer to interact with MXenes terminated with a specific type of functional groups. Thus, engineering MXene surface chemistry is crucial in order to achieve electrodes with a good affinity to Li$_2$S$_n$ species.

Second, although the electrochemical performances of Li-S batteries have been efficiently improved by introducing MXenes, some of the properties are achieved at a low sulfur loading or tap density. Thus, the areal and volumetric capacities are typically low at the current stage. Future studies should pay attention to the construction of high S loading electrodes with a high tap density. As such, MXene-based Li-S batteries with superior properties are expected.

Third, in line with the fast development of portable and wearable electronic devices, the power sources should also be lightweight and flexible enough (even foldable) without compromising their charge-storage performances. To this end, exploring facile and low-cost techniques to construct electrodes with robust structure and high mass loading are meaningful for new type MXene-based Li-S batteries and beyond.

Finally, as a new class of 2D wonder materials, MXenes are not just Ti$_3$C$_2$Tx. To date, more than 30 MXene phases have been reported with more predicted to exist. There are certainly enough incentives to explore other MXene members for high-performance Li-S batteries. Moreover, through tuning the physical and chemical properties of existing MXenes under the guide of theoretical simulations, there is certainly much room available for the reported MXene-S systems to further boost their electrochemical performances in Li-S batteries. We firmly believe that, through the collective efforts from all over the world, MXene-S based Li-S batteries will finally come to our daily life, just give it enough time.

**ACKNOWLEDGMENTS**

C.Z., S.A., and J.H. would like to thank the support from an Empa interal research grant.

**CONFLICT OF INTEREST**

The authors declare no conflict of interest.

**ORCID**

Chuanfang (John) Zhang https://orcid.org/0000-0001-8663-3674

**REFERENCES**


62. Dillon AD, Ghidu MJ, Krick AL, et al. Highly conductive optical quality solution-processed films of 2D titanium car-


AUTHOR BIOGRAPHIES

Chuanfang (John) Zhang completed his PhD program in East China University of Science and Technology (Shanghai, China) and Drexel University (Philadelphia, PA) in 2015 under the joint supervision of Prof. Yury Gogotsi. In 2015, he joined Trinity College Dublin, Ireland as a research fellow. He joined Empa, ETH Domain, as a senior scientist, working on the additive manufacturing of printed electronics based on multifunctional two-dimensional crystal inks. He serves as a reviewer for 32 peer-review journals, such as Nature Comm., Joule, JACS, EES, AM, ACS Nano, AEnM, Small, EnSM, Nano Energy, and so forth. He has published ~50 cutting-edge studies on top journals, including Springer Nature (book chapter), Nature Energy, Nature Communications, Adv. Mater (VIP), Adv. Funct. Mater (VIP), ACS Nano, Nano Energy, and so forth. His H-index is 29 with SCI citations >3300. He has given >70 invited talks in universities/major conferences/companies. He was shortlisted 2016 and 2018 Irish Lab Scientist of the Year, Lab Staff Member of the Year and Young Leader of the Year (Ireland). He is the recipient of “2019 Top 10 Chinese Leading Talents in Science and Technology in Europe.”

Linfan Cui received her PhD degree in Chemistry from Beijing Institute of Technology under the supervision of Prof. Liangti Qu, in 2019. In 2018, she studied as a visiting PhD in A.J. Drexel Nanomaterials Institute and Department of Materials Science and Engineering at Drexel University under the guidance of Prof. Yury Gogotsi. She is currently a postdoctoral researcher in the Department of Electronics and Nanoengineering (Prof. Harri Lipsanen group), Aalto University, Finland. Her research interests lie in the development of new methods and strategies to synthesize 2D functional materials for various applications.

Jakob Heier graduated in physics from Konstanz University (Germany) and received a Ph.D. in Materials Science and Engineering from Cornell University (NY) in 1999. Jakob Heier is group leader in the Laboratory for Functional Polymers at the Swiss Federal Laboratories for Materials Science and Technology (Empa). His research focusses around self-assembly phenomena related to thin film formation from solution. Along this line, he is heading the large-area wet coating and printing activities of EMPA’s Coating Competence Center.

How to cite this article: Zhang C(J), Cui L, Abdolhosseinzadeh S, Heier J. Two-dimensional MXenes for lithium-sulfur batteries. InfoMat. 2020; 2:613–638. https://doi.org/10.1002/inf2.12080