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To cite this version:

Zifeng Lin, Hui Shao, Kui Xu, Pierre-Louis Taberna, Patrice Simon. MXenes as High-Rate Electrodes for Energy Storage. Trends in Chemistry, 2020, 2 (7), pp.654-664. 10.1016/j.trechm.2020.04.010 . hal-03105841

HAL Id: hal-03105841

https://hal.science/hal-03105841

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Lin, Zifeng and Shao, Hui and Xu, Kui and Taberna, Pierre-Louis and Simon, Patrice *MXenes as High-Rate Electrodes for Energy Storage*. (2020) Trends in Chemistry, 2 (7). 654-664. ISSN 2589-5974

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MXenes as High-Rate Electrodes for Energy Storage

Zifeng Lin,[1] Hui Shao,[2,3] Kui Xu,[4] Pierre-Louis Taberna,[2,3] and Patrice Simon[2,3,5,*]

Two-dimensional transition-metal carbides/nitrides, namely MXenes, are gaining increasing interest in many research fields, including electrochemical energy storage. This short review article emphasizes some recent breakthroughs achieved in MXene chemistry and electrochemical performance when used as high-rate electrodes, especially in nonaqueous electrolytes. Lastly, the current limitations and future perspectives are highlighted.

Highlights

MXenes are 2D materials that offer great promise for electrochemical energy storage. While MXene electrodes achieve high specific capacitance and power rate performance in aqueous electrolytes, the narrow potential window limits the practical interest of these systems.

The development of new synthesis methods to prepare MXenes, such as by using a molten salt approach, broadens the variety of precursors that can be used. In addition, these methods allow for tuning the nature and content of the surface functional groups present at the MXene surface.

Recent studies reported high performance for MXene electrodes in nonaqueous electrolytes with both high capacity, high voltage, and fast charge–discharge rate. Those performances, ascribed to the control of the MXene/electrolyte interface, offer new opportunities for designing the next generation of high-rate materials for energy storage applications.

The Rise of MXenes

MXenes are 2D materials with the formula of $M_{n+1}X_nT_x$, where M represents the transition metal(s), X is carbon and/or nitrogen, and T_x stands for the surface terminations (e.g., –OH, –O, –F, and so on) that are introduced during chemical preparation such as those presented in Figure 1A,B [1]. Since the first discovery of the $Ti_3C_2T_x$ MXene in 2011, MXenes have expanded significantly as a novel 2D materials family containing almost 30 members with different chemical compositions and order [2]. Typically, MXenes are prepared by selective etching of the A elements from the MAX phase precursors via a HF-containing solution. Considering the rich chemistry of the MAX phase precursors as presented in Figure 1A (more than 150 MAX available today) [3–5], new MXenes are being discovered routinely. Thanks to their tunable properties (e.g., surface chemistry, conductivity, and 2D structure), MXenes are promising for many applications, including energy storage and conversion, catalysis, sensing, electromagnetics, optics, and water purification, among others [6]. However, the most promising applications deal with electrochemical energy storage, including metal-ion batteries and electrochemical capacitors (ECs) [7].

In recent years, MXenes have afforded major advances in the field of ECs, including the design of new ultra-high capacitance MXene electrodes and understanding of charge-storage mechanisms. This short review focuses on the electrochemical behavior of MXene electrodes in aqueous and nonaqueous electrolytes for energy-storage applications. The state-of-the-art findings of the intercalation pseudocapacitance of the MXene electrode in lithium- or sodium-containing organic electrolytes will be also described, which paves the way for preparing high energy-density MXene-based ECs for practical applications.

Advancements in MXene Chemistry

Different from the well-known 2D graphene or other 2D materials that are stacked and held together by van der Waals interactions and are easily exfoliated from their corresponding precursors, the chemical bonds between the $M_{n+1}X_n$ layer and A element layer of MAX phases are much stronger, resulting in difficulties for preparing MXenes via mechanical exfoliation. However, the bonding of M–X atoms is much stronger than that of the M–A atoms [8], enabling the possibility of selective removal of the A element with specific chemical etchants. In 2011, Gogotsi, Barsoum, and colleagues first reported the synthesis of $Ti_3C_2T_x$ (the first MXene), prepared by selective etching of Al-layers from the Ti_3AlC_2 MAX phase precursor immersed in HF solution [9]. Later, alternative acidic solutions were proposed as etching baths, such as the mixture of hydrochloric acid (HCl) with lithium fluoride (LiF) [10], HCl with sodium fluoride (NaF) [11], ammonium hydrogen

[1]College of Materials Science and Engineering, Sichuan University, No. 24 South Section 1, Yihuan Road, Chengdu 610065, PR China
[2]CIRIMAT, Université de Toulouse, CNRS, CIRIMAT, 118, Route de Narbonne, 31062 Toulouse Cedex, 9, France
[3]Réseau sur le Stockage Electrochimique de l'Energie (RS2E), Fédération de Recherche CNRS 3459, HUB de l'Energie, Rue Baudelocque, 80039 Amiens, France
[4]Key Laboratory of Flexible Electronics (KLOFE) and Institute of Advanced Materials (IAM), Jiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211816, PR China
[5]Institut Universitaire de France, 1, Rue des Ecoles, 75005 Paris, France

*Correspondence: simon@chimie.ups-tlse.fr (P. Simon).

https://doi.org/10.1016/j.trechm.2020.04.010

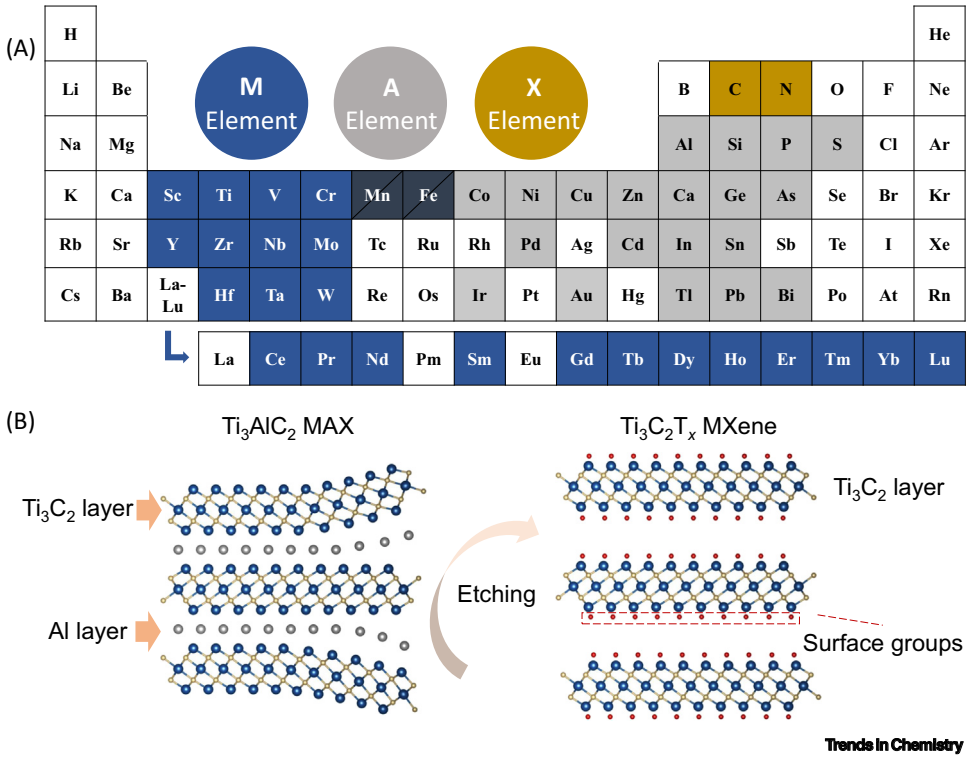

Figure 1. The MAX Phase and MXene Chemistry. (A) Periodic table of the elements showing the updated MAX phase compositions, including the recently reported novel MAX phases with A = Co, Ni, Cu, Zn, and so on; Mn and Fe may appear in either M or A position [4,5]. (B) Schematic showing the etching of Ti_3AlC_2 MAX phase precursor into $Ti_3C_2T_x$ MXene.

fluoride (NH_4HF_2) [12], and ammonium dihydrogen fluoride in organic polar solvents [13]. To avoid the use of hazardous HF-containing solutions, other methods such as hydrothermal treatment in aqueous sodium hydroxide (NaOH) solution [14] or thermal-assisted electrochemical etching [15] were developed. While these methods can be successfully used for Al-containing MAX phases (Al as the A element), as presented in Figure 1A, other MAX phases (with A = Si, Ga, Ge, Sn, and so on) are still difficult to etch. Some progress has been made, such as the successful etching of the Ti_3SiC_2 MAX phase by a HF solution containing H_2O_2 [16]. Recently, Li and colleagues [17] reported a method to prepare 2D MXenes from a broad range of MAX-phase precursors, with A elements Al, Si, Ga, and Zn, based on the MAX precursors etching in F-free Lewis acid **molten salts** (see Glossary). Interestingly, theoretical calculations show the possibility of preparing MXenes from unexplored MAX phases by a careful selection of the Lewis acid salts, which exhibit a redox potential higher than that of the corresponding A elements. This method sheds light on the opportunity to further enrich the MXene family.

Also important to note is that a change in the synthesis route of MXenes may result in a noticeable difference in surface terminations [18]. For instance, the surface terminations of HF- or HCl/LiF-etched MXenes mainly contain -O, -OH, and -F. Quantitative NMR spectroscopy has shown that HF-synthesized $Ti_3C_2T_x$ MXene exhibit almost four times -F termination as well as more -OH and less -O terminations compared with the same $Ti_3C_2T_x$ MXene prepared in a mixture of HCl/LiF solution [19]. Even using the same method with different HF concentrations may result in the variation in surface termination composition [20]. MXenes prepared by NaOH hydrothermal treatment [14] or electrochemical etching [15] show no -F termination on the surface, and Lewis

acid molten salts-derived MXenes present mainly -Cl and -O surface terminations [17]. Annealing treatment of MXenes under vacuum or various gas atmospheres is an effective route to manipulate surface terminations [21–24]. Persson and colleagues reported the possibility of defluorination by heating under vacuum conditions and further fully terminated with oxygen by exposure to oxygen gas at 450°C [24]. Both theoretical and experimental investigations show that the change in surface chemistry has important effects on the resulting physical or chemical properties (e.g., conductivity and chemical redox activity) [21,23,25]. For instance, the hydrophilicity of MXenes depends greatly on the surface terminations: MXenes prepared by HF or HCl/LiF are typically hydrophilic due to the existence of -OH or -O functional groups [1,10], which can be turned hydrophobic by further removal of these groups upon thermal treatment [26].

Most MXenes exhibit a metal-like conductivity; some semimetallic or semiconducting MXenes have also been identified, depending on the nature of M elements and the surface terminations [25]. $Ti_3C_2T_x$ spin-cast MXene films exhibit a high conductivity of about 10^4 S cm^{-1} [27]. Another key feature making MXenes attractive candidates for EC electrodes is their unique 2D structure with open accordion-like morphology and high specific surface area, which allows for fast charge transport and high surface charge accumulation.

MXenes as EC Electrodes in Aqueous Electrolytes

Unsurprisingly, the first discovered MXene, $Ti_3C_2T_x$, is to-date the most studied. In 2013, Gogotsi and colleagues reported successful accommodation of a large variety of cations, including Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, and Al^{3+}, in a $Ti_3C_2T_x$ MXene electrode, from neutral and alkaline aqueous electrolytes. A volumetric capacitance exceeding 300 F cm^{-3} was achieved, corresponding to about three times that of conventional porous carbons [28]. The symmetric and rectangular-shaped voltammograms observed in various alkaline and neutral electrolytes (Figure 2A and Box 1), without marked redox peaks, indicate a typical capacitive electrochemical signature. Moving to acidic aqueous electrolytes, Ghidiu and colleagues reported capacitances up to 900 F cm^{-3} (245 F g^{-1}) in 1 M H_2SO_4 electrolyte without significant degradation over 10 000 cycles [10]. An exceptional high capacitance of 1500 F cm^{-3} (370 F g^{-1}) was further achieved within a 1-V potential range, outperforming the best reported pseudocapacitive or capacitive electrode materials in aqueous electrolytes [29]. As presented in Figure 2B, a pair of redox peaks were observed on the **cyclic voltammetry (CV)** profiles, indicating the pseudocapacitive nature of the $Ti_3C_2T_x$ MXene electrode in acidic aqueous electrolytes. *In situ* X-ray absorption spectroscopy measurements further evidenced the variation of the Ti oxidation state of the $Ti_3C_2T_x$ MXene electrode during electrochemical polarization, confirming the pseudocapacitive charge-storage mechanism [30]. Further studies by Hu and colleagues revealed that hydronium in the H_2SO_4 electrolyte (de)bonds with the terminal -O in the $Ti_3C_2T_x$ MXene electrode upon discharging(charging) that gives rise to the change of oxidation state of titanium [31]. In addition to the high capacitance and enlarged potential window, the extremely high-rate performance was achieved by controlling the electrode porous structure to enhance electrolyte accessibility to the MXene surface. The macroporous $Ti_3C_2T_x$ MXene electrode (Figure 2C) can still deliver a capacitance of 210 F g^{-1} at 10 V s^{-1} [29]. Designing vertically aligned $Ti_3C_2T_x$ MXene flakes onto the current collectors could further boost the rate performance, as shown in Figure 2D. The electrode architecture greatly shortens the ion transport pathway as compared with a conventional filtered film electrode. As a result, CV profiles in Figure 2E clearly evidence the excellent performance of a vertically aligned $Ti_3C_2T_x$ MXene electrode, even with an electrode thickness up to 200 μm [32]. In addition to $Ti_3C_2T_x$ MXene, other MXenes such as Ti_2C, Mo_2C, $Mo_{1.33}C$, V_2C, and so on, were also investigated in aqueous electrolytes and fascinating electrochemical performance was reported [33–37]. For example, VahidMohammadi and colleagues showed that V_2CT_x MXene electrodes are able to deliver high gravimetric (~400 F g^{-1}) and volumetric (~1300 F cm^{-3}) capacitance in H_2SO_4 electrolytes, even surpassing the performance of $Ti_3C_2T_x$

Glossary

Cyclic voltammetry (CV): a widely used electrochemical technique. The principle is to apply a linear voltage ramp to an electrode (or a device) between two voltage limits and measure the resulting current.

Energy density: the amount of energy stored in a given energy storage device normalized with the mass or volume. The SI unit is J/m^3 or J/kg (Wh/l, Wh/kg are commonly used for batteries and supercapacitors).

Galvanostatic charge–discharge (GCD): an electrochemical technique of applying a constant to charge/discharge the electrochemical cell or electrode within the control potential range.

Ionic liquids: salts composed solely of ions with melting points below 100°C.

LP30: 1.0 M lithium hexafluorophosphate (Li-PF_6) in ethylene carbonate (EC) and dimethyl carbonate (DMC) organic solvents with a volume ratio of 1:1.

Molten salts: salts composed solely of ions, but with higher melting points.

Specific capacitance: capacitance is the ratio of the charge change of a system to the corresponding potential change. In supercapacitors, capacitances of the electrode (or cell) are typically normalized with the electrode (or cell) mass, volume, and areal, which are termed as specific gravimetric, areal, and volumetric capacitance, respectively.

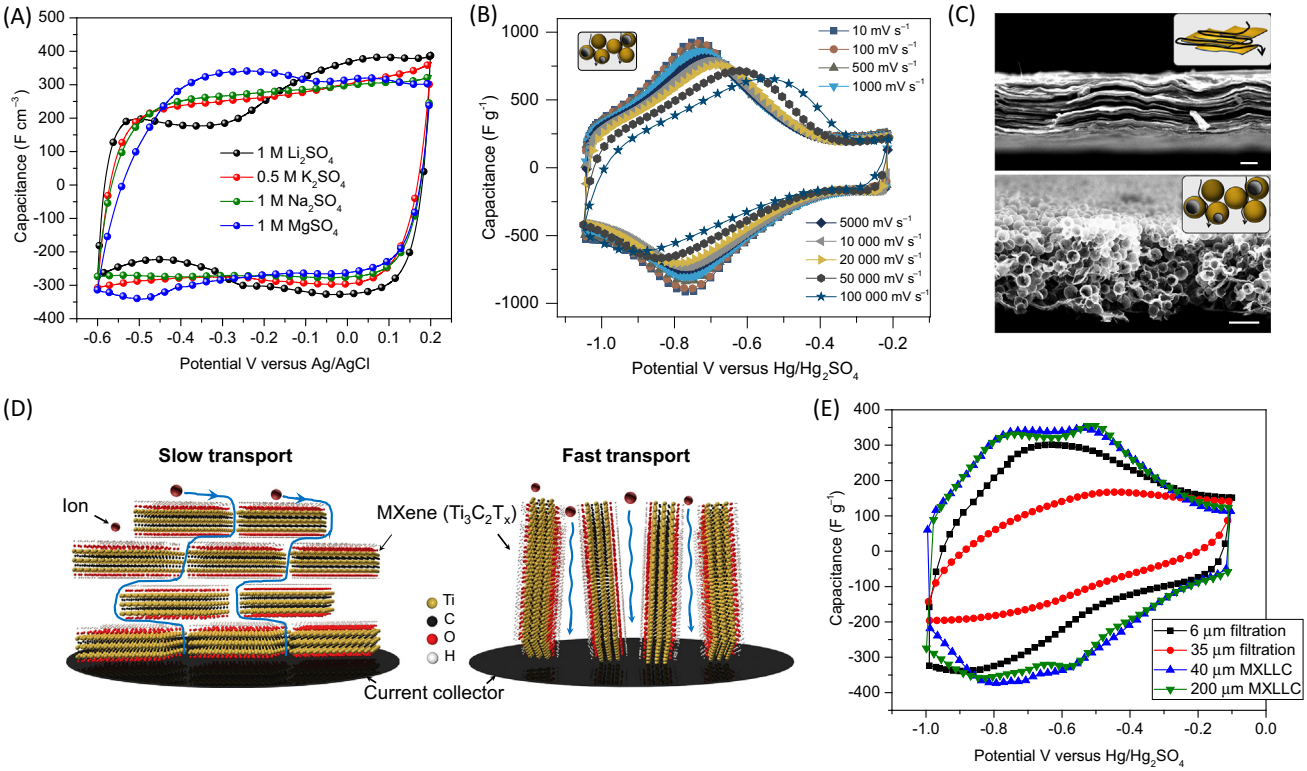

Figure 2. Electrochemical Signature of MXenes in Aqueous Electrolytes. (A) Cyclic voltammograms at 2 mV s^{-1} for a 25-µm-thick d-$Ti_3C_2T_x$ paper electrode in sulfate aqueous electrolytes. (B) Cyclic voltammetry data collected at scan rates from 10 to 100 000 mV s^{-1} for a 90-nm-thick $Ti_3C_2T_x$ MXene. (C) Scanning electron microscopy images of a (top panel) $Ti_3C_2T_x$ MXene hydrogel cross-section and (bottom panel) macroporous templated $Ti_3C_2T_x$ electrode cross-section. Scale bars: 5 µm. Insets show a schematic representation of the ionic current pathway in electrodes of different architectures. (D) Schematic illustration of ion transport in horizontally stacked and vertically aligned $Ti_3C_2T_x$ MXene electrodes. (E) Cyclic voltammograms of the indicated samples at a scan rate of 100 mV s^{-1}. Adapted, with permission, from [1,28,29,32].

electrodes in similar electrolytes [33]. These results highlight the importance of developing a larger portfolio of MXenes with appealing properties and shed light on the promising future of MXenes for capacitive energy storage.

However, a limitation comes from the narrow potential window, limited on one hand to the hydrogen evolution reaction in the negative potential range and on the other hand to MXene oxidation at higher anodic potentials. As a result, despite high **specific capacitance** performance, the maximum **energy density** E ($E = ½\, C{\cdot}V^2$, where C is the capacitance and V is the maximum operating voltage) still falls short.

MXenes as High-Rate Electrodes in Nonaqueous Electrolytes

A direct approach to broaden the cell voltage is to move from aqueous to nonaqueous electrolytes. Generally, nonaqueous electrolytes, including organic and **ionic liquid** electrolytes that are stable within a potential window up to 3 V (or higher). Conventional organic electrolytes for ECs consist of acetonitrile (ACN) or propylene carbonate (PC) as solvents and conducting salts (e.g., Et_4N-BF_4, Pyr-FSI, EMI-TFSI, and EMI-BF_4). In the past few years, mixtures of carbonates in combination with lithium or sodium salts that are typically used as electrolytes in lithium- or sodium-ion batteries have been proposed as electrolytes for ECs as well.

Box 1. Batteries and Electrochemical Capacitors (ECs)

ECs include electrical double-layer capacitors (EDLCs) and pseudocapacitors. EDLCs store charge through electrostatic adsorption/desorption of charge carriers on porous electrodes and electrolyte interfaces, while pseudocapacitors store charge mainly through redox reactions of electrode materials with electrolytes. Batteries use diffusion-limited electrochemical oxidation-reduction (redox) reactions to store the charge, where phase transition in the materials is usually achieved during charge–discharge. Current batteries include lithium-ion, sodium-ion, and zinc-ion batteries (under development), while potassium-ion, aluminum-ion, and magnesium-ion batteries are currently at the research stage. As recently discussed by Mathis and colleagues [58], capacitive/pseudocapacitive systems can be distinguished from battery-like materials by comparing their electrochemical signatures, such as cyclic voltammograms (CVs) and **galvanostatic charge–discharge (GCD)**. EDLC electrode materials typically show a linear voltage versus time response (a triangular-shaped profile) during constant current charging/discharging (Figure IA) and rectangular CVs (Figure ID). A constant capacitance is achieved in the full potential range. However, battery-type electrode materials show obvious plateaus during GCD profiles (Figure IC) or sharp, clearly separated oxidation and reduction peaks (Figure IF) in CV curves. In such cases, the use of capacitance (*F*) is meaningless since a capacitance defines a constant change of the charge *Q* (As) in a potential window *V* (Figure IA). The capacity *Q* (A·s) has then to be employed for this general case. Pseudocapacitance, also called 'redox capacitance', is a charge storage mechanism involving fast, nondiffusion limited redox reactions. When the storage is limited to the surface, pseudocapacitive materials show box-like CV response (RuO_2, MnO_2); the capacitance (*F*) can then be used to define the electrochemical behavior. When these fast, nondiffusion limited redox reactions occur within the bulk of the material, they are termed intercalation pseudocapacitance. Materials like MXenes [29], Nb_2O_5 [45], and WO_3 [59], show a sloping discharge profile (Figure IB) and CVs with the presence of broad, symmetric redox peaks (Figure IE). In these cases, the use of capacity *Q* (As or mAh) is recommended to account for the redox nature of the charge storage. There are also many methods that have been proposed to categorize the electrode by examination of the material's intrinsic charge storage kinetics [58,60–62].

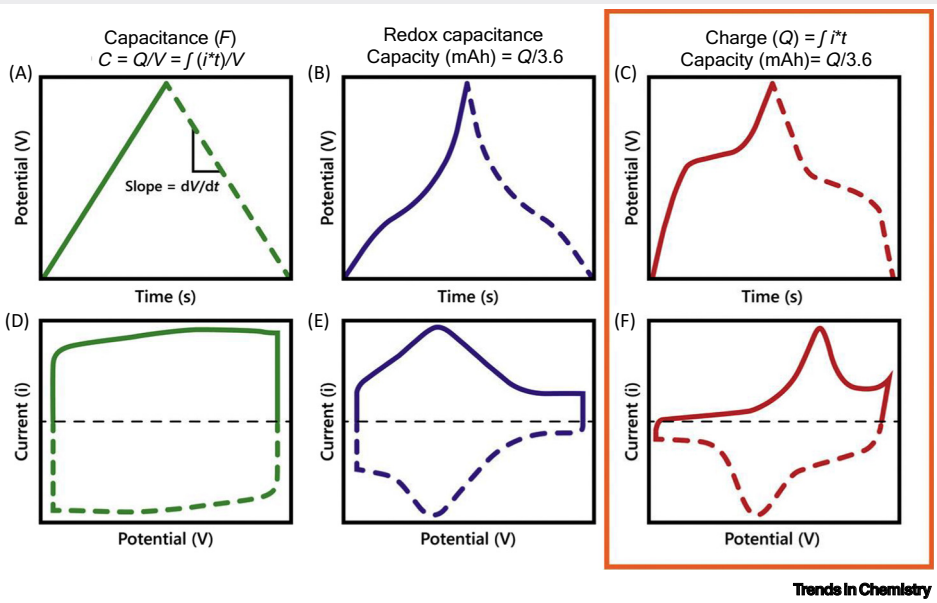

Figure I. Archetypal Electrical Output Behavior of Three Main Types of Electrodes, Including (A,D) Electrical Double Layer, (B,E) Pseudocapacitive, and (C,F) Battery Type. (A–C) Schematic of galvanostatic charge–discharge profiles showing linear and nonlinear responses with time and (D–F) corresponding cyclic voltammetry profiles. Adapted, with permission, from [58].

In Conventional Nonaqueous Electrolytes

Early efforts devoted to the investigation of MXenes in conventional nonaqueous electrolytes achieved a significant extension of the potential window [38–40]. In 2015, Dall'Agnese and colleagues tested MXene/carbon nanotube (MXene/CNT) composite electrodes in several organic electrolytes, including 1 M EMI-TFSI, 1 M EMI-BF_4, and 1 M TEA-BF_4 in ACN [40]. A potential win-dow of 1.8 V was achieved, together with a limited maximum capacitance of 80 F g^{-1} (245 F cm^{-3}).

CNTs were used here to avoid the restacking of the MXene electrode film obtained by vacuum filtration and enhance the accessibility of the MXene surface to electrolyte ions, including those of large size. Interestingly, a pair of redox peaks were observed, which could be ascribed to the intercalation of cations. Later on, Lin and colleagues [39] prepared a $Ti_3C_2T_x$ MXene electrode preintercalated with a neat ionic liquid electrolyte (EMI-TFSI) that could deliver high power capability within a 3 V voltage window with a capacitive electrochemical signature; however, the capacitance was still limited and reached only 80 F g^{-1}. Moreover, similar redox peaks were also observed in the CV profiles of the electrode when tested in a three-electrode cell set-up, as presented in Figure 3A. Further *in situ* X-ray diffraction (XRD) analysis indicates the reversible expansion of interlayer spacing during negative polarization, while a reversible shrinkage occurs during positive polarization. Such behavior was explained by the reversible (de)intercalation of EMI^+ cations at the $Ti_3C_2T_x$ negative electrode and EMI^+ cation/$TFSI^-$ anion exchange at $Ti_3C_2T_x$ positive electrode (Figure 3B) [41,42]. This charge-storage mechanism was later confirmed by molecular dynamic simulations [43]. In addition, by combining electrochemical dilatometry together with *in situ* XRD measurements, Jäckel and colleagues demonstrated a highly reversible swelling/contraction of Ti_3C_2-MXenes in two different neat ionic liquids (EMI-TFSI and BMIM-BF_4). Figure 3C,D presents the

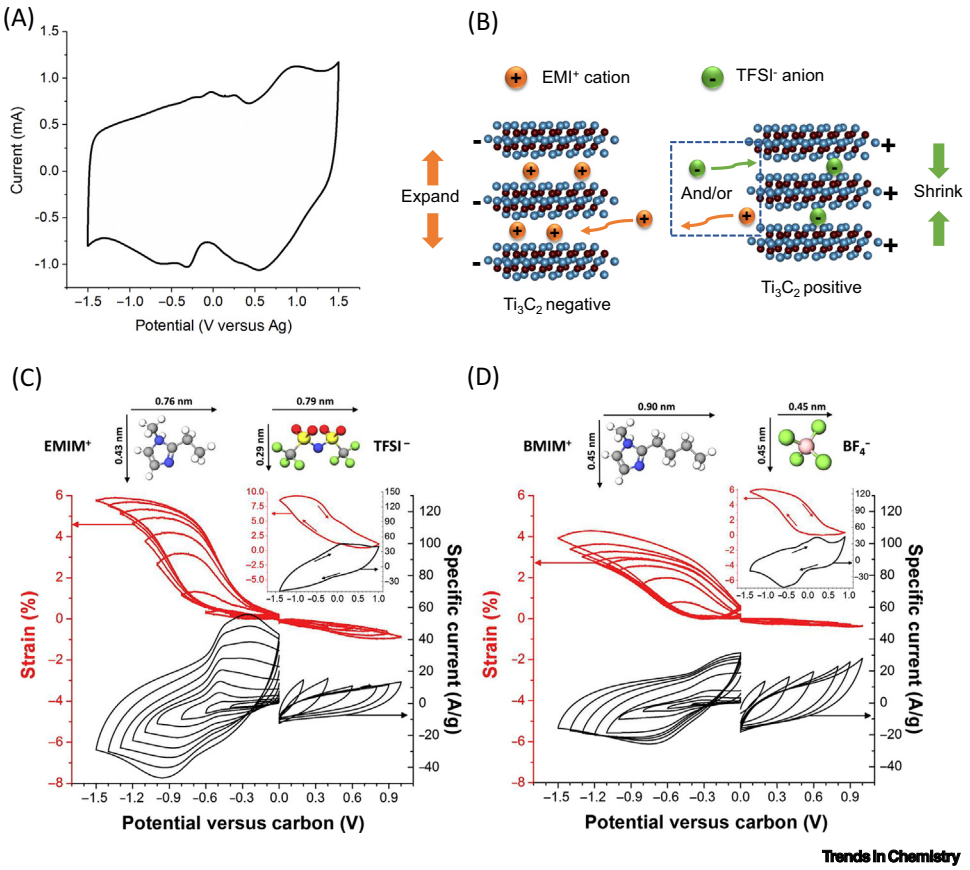

Figure 3. MXene Electrochemical Capacitor (EC) Electrodes in Conventional Nonaqueous Electrolytes. (A,B) $Ti_3C_2T_x$ electrodes in neat EMI-TFSI ionic liquid electrolyte. (A) Cyclic voltammetry (CV) profile of at 20 mV s^{-1} in the –1.5 to 1.5 V versus Ag potential range. (B) Schematic of the charge storage mechanism–cation insertion at negative polarization and cation desertion and/or anion insertion at positive polarization. (C,D) Combination of *in situ* electrical dilatometry and cyclic voltammetry at 1 mV s^{-1} sweep rate. The expansion/contraction is normalized to the equilibrium thickness (after 24 h) at 0 V versus carbon. (C) In EMI-TFSI and (D) in BMIM-BF_4. Insets: full-range CV with related displacement with arrows indicating the direction of potential sweeping. Adapted, with permission, from [41,42,44].

strain evolution of the MXene electrode during CV tests in two ionic liquids that confirm much larger stain during cation insertion under negative polarization, in comparison with cation/anion swapping during positive polarization [44]. Recently, Zheng and colleagues used ionic liquid preintercalated MXene films as electrodes to prepare ionogel-based flexible micro-supercapacitors (MSCs) [38]. MSCs could achieve a cell voltage of 3 V, together with volumetric and areal energy density among the highest values reported for MSCs (43.7 mWh cm^{-3} and 13.9 μWh cm^{-2}, respectively).

To summarize, limited attention has been focused on MXene-based ECs in conventional organic or ionic liquid electrolytes, which have the potential to change the game because of the large voltage windows associated with nonaqueous electrolytes. Although larger potential windows up to 3 V can be obtained, the specific capacitance is still limited as compared with those achieved in aqueous electrolytes. A possible explanation is the restacking of the MXene flakes, resulting in narrower interlayer spacing and consecutive limited cation/anion access to the interlayer space between the MXene sheets. Fine-tuning the interlayer spacing or designing a specific electrode structure adapted to the electrolyte may appear as effective routes to enhance the performance in these electrolytes. Another promising strategy is to unlock the redox activity of MXenes in nonaqueous electrolytes as observed in aqueous acidic electrolytes.

In Metal Ion-Containing Organic Electrolytes

As reported by Dunn and colleagues, some metal oxides, such as α-MoO_3 and T-Nb_2O_5, can act as a lithium storage host via ultrafast lithium-ion (de)intercalation in Li-ion battery electrolytes, without diffusion limitations [45,46]. Those materials offer great promise to enhance the rate capability (in charge and discharge) of Li-ion batteries. Considering their accordion-like open structure and metallic conductivity, MXenes were expected to be good candidates for fast Li-ion intercalation. As a result, since the first publication of MXenes by Naguib and colleagues from M. Barsoum's and Y. Gogotsi's groups, they have been studied as a negative electrode for Li-ion battery applications [47–50]. Figure 4A shows a typical CV of a Ti_3C_2 MXene electrode prepared from etching in HF- or F-containing solution (noted as HF-MXene) [50]. The lithium intercalation/deintercalation reaction (Figure 4A) occurs within the full potential window, that is, from 0.05 V up to 3 V versus Li^+/Li, and is achieved in a sequential way through several steps [50]. The CV shows two different sets of peaks visible at 2.53/2.45 V versus Li^+/Li and 1.00/0.97 V versus Li^+/Li. According to the previous study [50], where combined electrochemical tests and *in situ* XRD study were achieved, the set of redox peaks at high potential corresponds to Li-ion intercalation in large interlayer space, while the peaks at low potential correspond to Li-ion intercalation in small interlayer space. However, the large operating potential window for a negative electrode, together with the high irreversible capacity at the first cycle, has so far drastically limited the interest of these HF-MXene materials in Li-ion battery applications.

MXenes have also been studied as a positive electrode for sodium-ion intercalation. Figure 4B shows the CV of a V_2C MXene electrode in 1 M Na-PF_6 in EC/DMC [51]. A set of redox peaks associated with Na^+ intercalation/deintercalation reaction are visible at about 2.5 V versus Na^+/Na, on top of a rectangle-shaped capacitive signature from 1 to 3 V versus Na^+/Na. A similar electrochemical process was also observed with the Ti_2C MXene electrode in 1 M Na-PF_6 in EC/DEC, where a reversible capacity of 175 mAh g^{-1} was delivered in the 0.1–2.3V potential range [52]. Kajiyama and colleagues found that the intercalation distance in MXene electrode is expanded by the first sodiation process because of desolvated Na^+ intercalation and solvent molecule penetration, which further act as pillars to stabilize the structure [53]. Porous MXene electrodes were also developed to accelerate ion transport in organic electrolytes [54–56]. To summarize, similar to Li-ion, Na-ion intercalation in MXene electrodes is mainly achieved within a large operating potential window, which is a concern for further use in Na-ion battery applications.

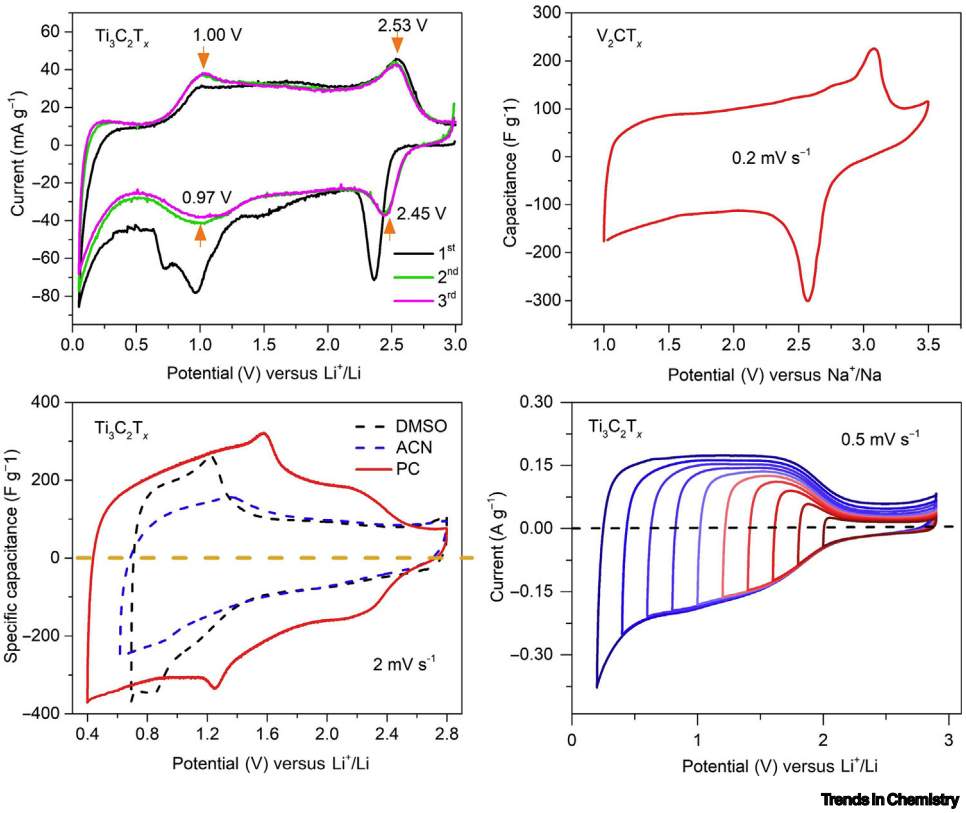

Figure 4. MXene Electrodes in Lithium or Sodium-Containing Organic Electrolytes. Cyclic voltammetry profiles of (A) $Ti_3C_2T_x$ in **LP30**; (B) V_2CT_x in 1 M $NaPF_6$ in EC/DMC (1:1); (C) $Ti_3C_2T_x$ in 1M Li-TFSI in DMSO, ACN, PC solvents, the original potential versus Ag wire is converted into potential versus Li^+/Li; (D) $Ti_3C_2T_x$ in LP30. Adapted, with permission, from [17,50,51,57].

A recent breakthrough was made by Wang and colleagues [57], who investigated the influence of various solvents on the charge-storage mechanism in a macroporous Ti_3C_2 MXene electrode, using the same 1M Li-TFSI salt concentration. As shown in Figure 4C, different CV signatures were obtained depending on the solvent (DMSO, ACN, and PC) used; surprisingly, the best electrochemical performance was obtained in PC-based electrolyte, with a capacity of 130 mAh g^{-1} at 2 mV s^{-1} within a 2.4 V voltage window. *In situ* XRD coupled with molecular dynamics simulations suggested that desolvated Li ions were intercalated between the MXene layers in PC-based electrolytes, leading to excellent electrochemical performance, 80 mAh g^{-1} being still delivered at charge/discharge rates of 1000 C. However, the co-intercalation of solvent molecules was evidenced together with Li^+ ions in DMSO and ACN systems due to the strong interactions between DMSO/ACN solvent molecules and Li^+ ions, which accounts for the limited electrochemical performance in these electrolytes. This study provides a rationale route by considering solvents as an effective strategy to improve the pseudocapacitive performance of MXene electrodes as well as other electrodes.

Finally, the latest advances have been made by Li and colleagues, who prepared MXene materials from a molten salt route (called MS-MXenes) [17]. Using a molten $CuCl_2$ Lewis acid as etching bath, they prepared MXene free of -F and -OH groups but with surface terminations only composed of -Cl and -O. The control of the MXene surface groups led to a remarkable electrochemical performance in a Li-ion battery electrolyte. The mirror-like CV profiles shown in Figure 4D differ from the previously reported pseudocapacitive signatures with at least some hump-like redox

peaks (Figure 4A–C). Instead, the charge storage mechanism in MS-$Ti_3C_2T_x$ MXene is achieved by an almost constant current during reduction and oxidation processes, similar to what is observed in a pseudocapacitive material, most of the capacity here being delivered below in the 0.2–2 V versus Li^+/Li potential range. The discharge capacity reaches a value as high as 205 mAh g^{-1} at 0.5 mV s^{-1}. Those remarkable performances make MXene materials now suitable to be used as negative electrodes in nonaqueous energy-storage devices.

Concluding Remarks and Future Perspectives

MXene chemistry is continuing to grow, with almost 30 compositions today and more being discovered routinely. Thanks to their key features (high accessible surface area and metallic-like electrical conductivity), 2D MXenes have emerged as promising candidates in many applications, one of the most promising being electrochemical energy storage. For instance, ultrahigh volumetric capacitance beyond 1500 F cm^{-3} can be achieved with Ti_3C_2 MXenes when used as EC electrodes in aqueous acidic electrolytes and high power can be obtained by designing specific 3D porous or vertically aligned MXene electrodes. However, the narrow potential window that can be reached in aqueous electrolytes limits the energy density of these devices and their further use in practical applications.

However, the fast, nondiffusion limited Li-ion intercalation observed with some metal oxides such as MoO_3 or Nb_2O_5 has revitalized the interest for studying MXenes in lithium or sodium organic electrolytes. While the nature of the solvents plays an important role in the charge-storage mechanism, the surface composition of MXene also has a strong impact on their reactivity and electrochemical performance. Various synthesis methods have then been proposed to tune the MXene surface chemistry to increase the electrochemical performance of MXenes in nonaqueous electrolytes. The recent report of a new MXene synthesis route using Lewis molten salts as an etching solution has already led to unique electrochemical signature and performance for lithium intercalation. These performances are assumed to originate from the tuning of the surface terminations (mainly -Cl, -O groups), as compared with the MXenes prepared by conventional methods containing -F, -OH, and O-rich groups. However, the road to success will need even more efforts in the following aspects (see Outstanding Questions):

(i) Taking the Lewis acid molten salt synthesis route as an example, environmentally friendly, safe, efficient, and scalable methods to broaden the MAX phases precursors and prepare MXenes with tunable surface compositions are needed.

(ii) About 70% of all MXene research work has focused on the first discovered MXene, which is $Ti_3C_2T_x$ [6]; other MXenes, although more difficult to prepare, must be investigated from both theoretical and experimental points of views.

(iii) Although MXene electrodes can achieve high capacitance in aqueous electrolytes, research efforts should be focused onto MXene in nonaqueous electrolytes considering the much wider potential window and recent promising results obtained. Fine-tuning the nature and content of MXene surface groups and controlling the interlayer spacing offer key opportunities for performance improvement.

(iv) To meet the simultaneous high-power and high-energy challenge of ECs and high-power batteries, designing 3D porous, vertically aligned, or other structured MXene electrodes to improve ionic transport paths in the electrode without scarifying too much the volumetric energy density is also an important research direction to develop in the few next years.

Outstanding Questions

How can we tune the synthesis process of MXene to have better control of the surface functional groups present on MXene surface?

Considering the strong influence of surface terminations on the electrochemical behavior of MXenes, how specifically do these functional groups affect the electrochemical process and performance?

In nonaqueous Li-ion battery electrolytes, what is the charge-storage mechanism at the origin of high rate performance (Li-desolvation)?

Despite the outstanding performance that has been achieved with $Ti_3C_2T_x$ MXene electrodes for electrochemical energy storage, and with the diversity of the MXene family, can other MXene materials deliver even better energy and power density?

Acknowledgments

Z.L. is supported by the Fundamental Research Funds for the Central Universities (YJ201886) and the National Natural Science Foundation of China (Grant No. 501902215). H.S. was supported by a grant from the China Scholarship Council (NO. 201608370077). P.S., P.L.T., and H.S. thank the Agence Nationale de la Recherche (Labex STORE-EX) for support.

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