Recent Advances in MXenes for Lithium-Ion Capacitors

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ABSTRACT: Recently, two-dimensional MXenes and MXene-based nanocomposites have become the most important electrode materials because of their unique physical and chemical characteristics. As the electrode of a lithium-ion capacitor, MXenes have exhibited metallic conductivity and plastic layer structure that provide more chemically active interfaces and shortened ion-diffusion lengths, and thus the unbalanced ion kinetics between the anode and cathode can be effectively alleviated. In order to further improve the electrochemical performance of MXenes, the composition, morphology and texture, surface chemistry, and structural configuration of MXenes are extensively investigated. In this mini-review, some recent research and progress of MXenes and MXene-based nanocomposites in lithium-ion capacitors are summarized, which focus on their nanostructure designs and chemical preparation methods, such as prepillaring MXenes, delaminated MXenes, and MXene-based hybrids. Finally, some future perspectives and critical challenges of MXene-based material for lithium-ion capacitor application are also presented and briefly discussed.

1. INTRODUCTION

Huge changes in the global climate and the shortage of fossil fuels require the society to acquire green and sustainable energy. Among various renewable storage devices, electrochemical energy storage (EES) devices stand out based on their high-energy efficiency and high performance. Thus, they have been extensively applied in portable electronic devices, smart grids, and hybrid electric vehicles (HEVs). The energy density for state-of-the-art lithium-ion battery (LIB) is about 200 Wh kg$^{-1}$. However, the intrinsic sluggish diffusion process of Li$^+$ into the bulk material impedes the power performance of LIBs (usually <2 kW kg$^{-1}$), which causes an inferior acceleration rate in HEVs. On the contrary, supercapacitors (SCs), which are known for their high power density (>10 kW kg$^{-1}$) and excellent cycling life (>10$^5$ cycles), suffer from unsatisfactory energy density (about 5–10 Wh kg$^{-1}$) since charge storage is mainly on/near the surface of porous materials. Hence, it is urgent to find an effective way to achieve a trade-off between LIBs and SCs.

In recent years, a new energy storage device lithium-ion capacitor (LIC), which is assembled by a LIB-type anode and a SC-type cathode with an appropriate electrolyte (contains lithium salt), has been a hot topic in the complementation of LIBs and SCs. The charge capture mechanism for the LIC is illustrated in Figure 1a. The energy storage and release for the conventional LIB-type materials are primarily derived from the insertion/deinsertion of the lithium ion, which are determined by the Li$^+$ diffusion rate into the bulk of material. Besides, PF$_6^-$ from the electrolyte is rapidly absorbed/desorbed on/near the surface of SC-type electrodes, and thus a considerable power density can be achieved. Up to now, various constructions of LICs have been reported with gratifying results. However, the obstacle for practical application of LICs is still huge due to the limited capacity of SC-type material and the imbalance of charge storage kinetic between the two kinds of electrodes. These inevitably lead to the capacity mismatch between the anode and cathode, resulting in a low energy density of the LIC. Therefore, the critical issue in developing high-performance LICs is to utilize suitable anode and cathode materials with matched kinetics.

So far, a variety of electrode materials have been exploited in the LIC devices. On account of the different Li-ion storage mechanisms, the anode materials for LICs can be divided into three categories. First, insertion-type materials, such as graphite, hard carbon, TiO$_2$, Li$_4$Ti$_5$O$_{12}$ (LTO), and Nb$_2$O$_5$, have the advantage of stable structure. However, the inferior capacity (<400 mAh g$^{-1}$) or high-voltage platform versus Li metal impedes the full energy utilization. Then the alloy-type (Sn, Sn, and Sn-based composites) and conversion-type (Fe$_3$O$_4$, CoO, MoS$_2$, and MnO$_2$) materials can deliver high theory capacity (>700 mAh g$^{-1}$). Nevertheless, the high irreversible capacity, huge volume variation, and poor kinetics of these materials cause severe electrode polarization and capacity decay during the long-term cycling. Hence, for LIC anode materials, the key issues are fixating on improving the electronic/ion conductivity and cycle stability. From this aspect, materials with well-designed or nanosized structure can effectively shorten the Li$^+$ diffusion path and improve the
electron transport. At present, carbonaceous materials such as activated carbon (AC), graphene, and carbon nanotubes (CNTs) are the frequently used materials in LIC cathodes. Among various SC-type materials, AC has received wide attention due to its high special surface area, simple preparation, and low cost. However, its large narrow and tortuous pore channels prevent the diffusion of the electrolyte ion, and the relatively low electron conductivity causes an inferior capacity. Thus, cathode materials with large surface area and suitable pore-size distribution can effectively improve the capacity and power performance of LICs.

Recently, two-dimensional (2D) materials have triggered a new round of research hotspots since their unique structure affords more access in contact with the electrolyte and improves the ion transport rate. Graphene, as the first successfully prepared 2D material, has the advantages of remarkably high conductivity, high surface area (∼2630 m²/g in theory), and excellent thermal stability. However, the low tap density and suffering from restacking of 2D graphene prevent it from suitable electrode materials for the LIC applications. MXenes, which are known as the rising star in advanced electrochemical energy storage. MXenes, including Ti3C2T x, Nb2CT x, and V2CT x, possess novel ultrathin surface and open-layer structure, which relieve the sluggish intercalation/deintercalation kinetics of Li ions. MXenes are always prepared by selectively extracting the A element layers (A is generally the main group IIIA or IVA) from the corresponding three-dimensional M n+1AX n (n = 1–3) phases (Figure 1b,c). MXenes have been extensively investigated in various applications, especially as a high-performance electrode in LIBs and SCs, which are ascribed to their metallic conductivity (up to 10⁵ S/m), high density (∼3.8 g/cm³), mechanical stability, and excellent hydrophilicity. Moreover, the abundant active sites and negatively charged surfaces of 2D MXenes result in the great capability of charge storage and release. Stimulated by these exciting properties, MXenes are becoming promising candidate materials for the next-generation LIC application, and plenty of infusive achievements based on MXenes have emerged. Hence, it is necessary to update the latest developments of MXenes or MXene-based materials.

In this mini-review, we are committed to summarizing the recent research progress of MXenes and their derivatives in advanced LIC devices. At first, a short introduction for the electrode materials of LICs is provided. Subsequently, we propose to give a comprehensive and vital summary of the latest advanced MXene or MXene-based materials, which are used as the electrodes for high-performance LICs. Finally, there are some critical challenges and outlooks of 2D MXene materials generalized to highlight the future direction of LICs.

2. APPLICATIONS TO LITHIUM-ION CAPACITORS

As a hybrid electrochemical full cell, the LIC needs a large-capacity anode with reversible Li⁺ intercalation to achieve advanced electrochemical energy storage. MXenes, including Ti3C2T x, Nb2CT x, and V2CT x, possess novel ultrathin and open-layer structure, which relieve the sluggish intercalation/deintercalation kinetics of Li ions. So, MXenes present nonideal battery behavior but are similar to a capacitor, which indicates their application in lithium-ion capacitors. Furthermore, the energy storage property, electronic transmission speed, and stability of MXenes are affected significantly by functional groups (−F, −OH, −O, −Cl) on the surface of MXene layers.

2.1. Ti3C2Tx MXenes. Ti3C2T x, the typical representative among MXenes, is extensively studied according to its metallic conductivity and great chemical stability in fluoride-based acidic solutions. Ti3C2T x is prepared through selectively etching Al layers from the Ti3AlC2 (MAX) in HF and LiF/ HCl. Therefore, various termination groups (−OH, −F, −O, −Cl), which affect its physical and chemical properties, are

Figure 1. (a) Energy-harvesting mechanism of LIC in the charging process. (b) Atomic structures of M2AX, M3AX2, and M4AX3 phases. (c) The fragment of the element that makes up the MAX phase of the general composition M n+1AX n in the periodic table. Fragment of the periodic table (reprinted with permission from refs 7–9).
carried out on the Ti$_3$C$_2$Tx surface. In addition, these functional groups are in between Ti$_3$C$_2$Tx layers and function as “pillars”, leading to an original interlayer spacing of 0.977 nm for the unmodified Ti$_3$C$_2$Tx. Moreover, the stable interlayer space facilitates the contact between the Ti$_3$C$_2$Tx surface and electrolyte ions. Yet, according to previous reports, the existence of “pillars” on the surface of Ti$_3$C$_2$Tx may reduce the storage capacity for Li+. When the Ti$_3$C$_2$Tx is used as an anode for the lithium half-cell, only 70−225 mAh g$^{-1}$ (gravimetric capacity) can be realized, and even the theoretical capacity of Ti$_3$C$_2$Tx is predicted to be 320 mAh g$^{-1}$. So, if the interlayer space of Ti$_3$C$_2$Tx is rationally increased and utilized, the ability of fast Li-ion (de)intercalation will be further improved. Meanwhile, the unbalanced ion kinetics between the faradaic battery-type anode and the nonfaradaic capacitive cathode in LICs will be reduced.

One effective solution is to use electrochemical active materials acting as pillars, which can effectively exploit the potential storage space and resolve the low capacity issue for unmodified Ti$_3$C$_2$Tx. Tang et al. prepared Ti$_3$C$_2$Tx@Fe$_2$O$_3$ nanocomposites via a kind of surfactant and then used them as an anode for the lithium half-cell, only 70−225 mAh g$^{-1}$ (gravimetric capacity) can be realized, and even the theoretical capacity of Ti$_3$C$_2$Tx is predicted to be 320 mAh g$^{-1}$. So, if the interlayer space of Ti$_3$C$_2$Tx is rationally increased and utilized, the ability of fast Li-ion (de)intercalation will be further improved. Meanwhile, the unbalanced ion kinetics between the faradaic battery-type anode and the nonfaradaic capacitive cathode in LICs will be reduced.

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Figure 2. (a) Schematic illustration of the synthesis procedure for the Ti$_3$C$_2$Tx@Fe$_2$O$_3$ nanocomposite. (b) SEM images of the Ti$_3$C$_2$Tx@Fe$_2$O$_3$ nanocomposite. (c–f) TEM and HRTEM image of the Ti$_3$C$_2$Tx@Fe$_2$O$_3$ nanocomposite. (g–l) Elemental mapping of the Ti$_3$C$_2$Tx@Fe$_2$O$_3$ nanocomposite. (m) Rate performances of Fe$_2$O$_3$, Ti$_3$C$_2$Tx, and Ti$_3$C$_2$Tx@Fe$_2$O$_3$ electrodes. (n) Schematic illustration of the charge-storage mechanisms for the Ti$_3$C$_2$Tx@Fe$_2$O$_3$/NS-DPC LIC device. (o,p) CV and charge–discharge curves of the LIC. (q) Cycling stability of the LIC at a current density of 5 A g$^{-1}$ (reprinted with permission from ref 23).
Even though stearyltrimethylammonium bromide (STAB)@Ti$_3$C$_2$ (50 °C−60 °C) has the largest interlayer space (2.708 nm), the high temperature causes the formation of partial TiO$_x$ on the surface of Ti$_3$C$_2$T$_x$ (Figure 3b). By immersing CTAB@Ti$_3$C$_2$ in SnCl$_4$ solution, CTA$^+$ can successfully integrate Sn$^{4+}$ into CTAB@Ti$_3$C$_2$ (Figure 3c,d) via an ion-exchange mechanism. The elemental mappings of Ti and Sn confirm that Sn$^{4+}$ is inserted in the interlayer space of CTAB@Ti$_3$C$_2$ (Figure 3e,f). Furthermore, an LIC is assembled with CTAB-Sn(IV)@Ti$_3$C$_2$ as the anode and AC as the cathode (Figure 3g). The CV curves of LIC are presented in Figure 3h. The deviation from the expected rectangular shape is caused by the different energy-storage mechanisms between the anode and cathode, but the shape can still maintain unchanged as the scan rates increase from 2 to 20 mV s$^{-1}$. The GCD profiles of CTAB@Ti$_3$C$_2$//AC LIC exhibit a symmetry triangular shape.
Shown in Figure 4a, Ti3C2Tₓ is delaminated into a few or single atomic layers.24 The facile functional groups (T) on the surface of Ti3C2Tₓ determine that the binding forces of the interlayer are weak hydrogen bonding and van der Waals force. It provides a fast ionic accessibility to redox centers, thus a high energy density of 105.56 Wh kg⁻¹ at the power density of 495 W kg⁻¹. Meanwhile, as shown in Figure 3j, the LIC can maintain 71.1% of initial capacity at the current density of 2 A g⁻¹ after 4000 cycles. Previous studies have revealed that the delaminated MXenes can store more charge than their multilayer counterparts.24 The facile functional groups (T) on the surface of Ti3C2Tₓ determine that the binding forces of the interlayer are weak hydrogen bonding and van der Waals’ force. It provides a higher possibility to acquire delaminated Ti3C2Tₓ through intercalating dimethyl sulfoxide (DMSO), tetrabutylammonium hydroxide (TBAOH), or cation into the interlayer space.25 Meanwhile, MXenes have good mechanical property that allow them to be shaped into thin films by rolling or vacuum filtration.9 The freestanding MXene films can be directly employed as the electrodes without other current collectors such as Cu and Al metals. This unique flexibility is very beneficial for reducing the overall mass of the device and preparing the flexible LICs. Yu et al. mixed a delaminated Ti3C2Tₓ with carbon nanotubes to fabricate a self-supporting film anode (Ti3C2Tₓ/CNT) for LIC. In order to obtain delaminated Ti3C2Tₓ, the cationic reagent TBA⁺ is used as an intercalation, and then ultrasonic treatment is employed.4 As shown in Figure 4a, Ti3C2Tₓ is delaminated into a few or single layer, and the edge of delaminated Ti3C2Tₓ is discovered to be curved (Figure 4b), which demonstrates that its flexibility is identical to that of graphene. Moreover, the delaminated Ti3C2Tₓ nanosheets and CNTs under the vacuum filtration conditions can prepare a free-standing electrode (Figure 4c). As a pillar, the CNT looks like fishing nets wrapping the delaminated Ti3C2Tₓ, which can prevent the restacking of Ti3C2Tₓ and increase its conductivity. The LIC, which is assembled by Ti3C2Tₓ/CNT as an anode and AC as a cathode, confirms an energy density of 67 Wh kg⁻¹ (based on the total mass of Ti3C2Tₓ/CNTs and AC). Even at a power density of 5.79 kW kg⁻¹, the energy density can still reach 19 Wh kg⁻¹. Furthermore, after 5000 cycles at 2 A g⁻¹, the capacity retention of LIC is 81.3%, and the Coulombic efficiency is nearly 100% during the cycling test (Figure 4f).

2.2. MₓXTₓ MXenes. The structure of MXenes can be represented via the general formula Mₓ₁X₁₋ₓTₓ.22 Compared to the M₃ (“M” chemistry) and M₄ structures, their Mₓ counterparts show higher Li-ion specific capacities because Mₓ has less layers (2 layers) compared with previous 5 and 7 atomic layers.23 Yamada et al. assembled a LIC device, which is comprised of the intercalation-type (LiNi₀.₅Mn₀.₅Co₁O₂) electrode and pseudocapacitive electrode (Ti3C2Tₓ).21 The relationship between various surface termination groups (T) on Ti3C2Tₓ and the interlayer distance (d_inter) is also analyzed. As shown in Figure 5a−c, different from etching in HF (7.7 Å), the Ti3C2Tₓ synthesized by LiF/HCl carries a longer d_inter (8.7 Å). The reason is the presence of the new component of the termination group (T = −Cl), and the d_inter for surface termination (T) combinations presents a continuous increase with the addition of −Cl. The enlargement of interlayer spacing offers a fast ionic accessibility to redox centers, thus exhibiting higher intercalation pseudocapacitance. As demonstrated in Figure 5d, 250 mAh g⁻¹ capacity of the Ti3C2Tₓ is much larger than that of LiF/HCl etching of Ti3C2Tₓ (150 mAh g⁻¹). In addition, the permeation of solvent molecules will further increase the interlayer space during the charging−discharging process. The rate performance of LICs is usually limited by the diffusion capacity of lithium ions. In this system,
the interlayer space is expanded with the embedding of $-\text{Cl}$, and the large interlayer space boosts the faster Li-ion diffusion. Thus, at a sweep rate less than 2 mV s$^{-1}$, the capacitance of diffusion control in Ti$_2$CT$_x$ (LiF/HCl) is the largest among various Ti$_n$C$_{n+1}$T$_x$ (Figure 5e). Therefore, Ti$_2$CT$_x$ (LiF/HCl) as the capacitor-type anode for LIC can provide a higher rate capability. A Li-ion hybrid capacitor is assembled as shown in Figure 5f, exhibiting a high capacity of 206 mAh g$^{-1}$ in a voltage window of 2.58 V, and 84% of capacity is maintained after the 100 cycles (Figure 5g). Meanwhile, the LIC displays an energy density (160 Wh kg$^{-1}$) at a power density (220 W kg$^{-1}$) based on the total active materials.

According to the experimental data of the lithium half battery, the specific capacities of Ti$_3$C$_2$T$_x$ and Ti$_2$CT$_x$ are less than that of Nb$_2$CT$_x$ and V$_2$CT$_x$. The delaminating process of Nb$_2$CT$_x$ often uses different chemical approaches than that of Ti$_3$C$_2$T$_x$. Olha et al. reported the delamination of Nb$_2$CT$_x$ using amine instead of DMSO. Then, the Nb$_2$CT$_x$ paper was obtained by mixing the delaminated Nb$_2$CT$_x$ suspension with CNTs and filtering through a polyester membrane. The Nb$_2$CT$_x$/CNT paper electrode shows a high volumetric capacitance of 325 F cm$^{-3}$. Ayeong et al. demonstrated three proof-of-concept type LICs based on TBAOH-delaminated Nb$_2$CT$_x$/CNT electrodes. The Nb$_2$CT$_x$/CNT can be paired with either a graphite anode or a LiFePO$_4$ cathode. Furthermore, a symmetric capacitor is assembled using the Nb$_2$CT$_x$/CNT electrodes as the anode and cathode (Figure 6a–i). Three type of LIC devices are capable of operating within a 3 V voltage window and delivering stabilized capacities of 43, 24, and 36 mA g$^{-1}$, respectively. Continuous cycling of LICs demonstrated long lifespan for all three types of LICs, and the volumetric energy densities of all LICs are 50–70 Wh L$^{-1}$ (based on the volume of electrodes), which exceed the energy density of the conventional LTO/AC LIC.

In general, all kinds of MXenes display a layered structure, and the skeleton atoms of MXenes follow the ABABA or ABCABC arrangement. Meanwhile, the terminated groups ($-\text{F}$, $-\text{OH}$, $-\text{O}$, et al.) on the surface of MXenes directly influence their chemical/physical properties and then determine the performance of MXenes in their applications. In the field of energy storage, MXenes are often used as a substrate and further improve the performance through a series of chemical modifications. Through analyzing the electrochemical data of LICs assembled using MXenes or MXene composites, the capacitance is mainly a diffusion-controlled contribution, and it is worth noting that the surface control contribution cannot be ignored. Therefore, MXene materials have shown great potential in the lithium-ion capacitors.

3. CONCLUSIONS AND OUTLOOK

In summary, searching the novel electrode materials for a lithium-ion capacitor plays a really important role in development of electrochemical energy storage. MXenes, as the new star in the family of 2D materials, have attracted increasing attention because of their metallic skeleton, structural varieties, and substantial surface termination groups. The 2D nature of MXenes provides large surface areas for lithium-ion storage and boosts the fast ion transport. It is observed that MXenes exhibit some potential as a substrate material for the lithium-ion-
For studying Na⁺, K⁺, Mg²⁺, and other metal-ion hybrid and MXene-based materials, which possess ideal 2D structure, LICs' preparation routes and structure designs of MXenes are summarized and discussed in detail. The main electrocapacitor systems assembled by MXenes or MXene composites are categorized into three types: (1) anchoring self-assembly, (2) insertion, and (3) anchoring. Although this paper is focused on the research of MXenes for chemical properties of these LICs are listed in Table 1.

The advantages of 2D MXenes for the structure-electrochemical property to be addressed. The main disadvantage of the lithium-ion capacitor is their low energy density (compared to batteries), and the unmodified MXene electrodes do not have considerable theoretical capacity. Thus, anchoring the active substance on the nanosheets or delaminating the multilayer to monolayer are the practical methods to improve the electrochemical performance of MXenes. Although abundant examples of 2D MXenes in energy-storage applications have been performed, there are still some underlying scientific issues for the structure-electrochemical property to be addressed. First, the indispensability of the fluoride based (HF and LiF) on the process of etchants increases the risk. Searching for safe and reliable preparation methods is beneficial to the future development of MXenes. Second, single-layer MXenes are fabricated by delaminating multilayered MXenes in order to expose more lithium-ion storage active sites, but the delaminated MXenes in aqueous solution show a trend of restacking due to electrostatic interaction. Although the introduction of other substances as pillars can expand the interlayer space of MXenes, these also reduce the contact area between MXenes and electrolyte that impede their intrinsic properties in some cases. Third, since MXenes are unstable under ambient conditions, most MXenes are easily oxidized and degraded during treatment. The exploitation of the MXene-based hybrid system, such as anchoring self-assembly, delamination, insertion, and anchoring, is impossible to completely isolate oxygen and water. Therefore, the chemical stability control of MXenes still needs further investigation. Fourth, because the surface termination groups of MXenes are diverse and uncontrollable, the ion kinetics and charge storage mechanism for MXenes remain not completely clear. Compared to the lithium-ion battery, the main advantage of LICs is its high power density, and the ion transport speed of the battery-type electrode directly determines the rate performance of the device. Thus, in-depth basic studies of the lithium-ion storage mechanism for MXenes are needed tremendously.

Many breakthroughs of MXene and MXene composites, which are used as lithium-ion capacitor electrodes, have emerged in the past few years. However, there is indeed a long way to go to find solutions that balance various performances such as energy density and power density, specific capacity, and life span. In order to address the challenges, innovative works and practical applications of electrochemical energy storage are still desirable to further explore.

### Table 1. Comparison of MXenes and MXene-Based Materials for LIC Applications

| materials | synthesis approach | capacity of anode | working voltage for LIC | electrochemical performance for LIC | cycle number and capacitance retention for LIC | ref |
|-----------|-------------------|------------------|-------------------------|-------------------------------------|---------------------------------------------|-----|
| Ti₃C₂T₁₀@Fe₃O₄ | surfactant | 1180 mAh g⁻¹ at 0.1 A g⁻¹ | 0.01–4 V 1 M LiPF₆ nonaqueous solution | 216 Wh kg⁻¹ at 400 W kg⁻¹ | 5000 (87%) | 23 |
| CTAB-Sn(IV)@Ti₃C₂ | liquid-phase immersion | 765 mAh g⁻¹ at 0.1 A g⁻¹ | 1–4 V 1 M LiPF₆ nonaqueous solution | 105.6 Wh kg⁻¹ at 495 W kg⁻¹ | 4000 (71.1%) | 5 |
| delaminated Ti₃C₂T₁₀/CNT | TBAOH delamination and filtration, etching by LiF/HCl | 489 mAh g⁻¹ at 50 mA g⁻¹ | 1–4 V 1 M LiPF₆ nonaqueous solution | 67 Wh kg⁻¹ at 258 W kg⁻¹ | 5000 (81.3%) | 4 |
| Ti₃C₂Tₓ | amine-oxidation delamination and filtration | 400 mAh g⁻¹ at 0.5 C | 0.4–4.2 V 1 M LiPF₆ nonaqueous solution | 160 Wh kg⁻¹ at 220 W kg⁻¹ | 100 (84%) | 21 |
| NbₓCTₓ/CNT paper | TiBAOH delamination and filtration | 270 mAh g⁻¹ at 50 mA g⁻¹ | 0–3 V 1 M LiPF₆ nonaqueous solution | 50–70 Wh L⁻¹ | – | 19 |
| delaminated NbₓCTₓ/CNT | TBAOH delamination and filtration, etching by LiF/HCl | 226 mAh cm⁻³ at 10 mV s⁻¹ | 0–2 V 1 M LiSO₄ aqueous solution | 20.7 μWh cm⁻² at 2.2 mW cm⁻² | – | 20 |

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