Progress in Natural Science: Materials International xxx (xxxx) xxx–xxx

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Contents lists available at ScienceDirect

Progress in Natural Science: Materials International

journal homepage: www.elsevier.com/locate/pnsmi

Review

MXene–2D layered electrode materials for energy storage

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ARTICLE INFO

Keywords:
MXene
2D materials
Electrochemistry
Battery
Supercapacitor

ABSTRACT

As promising candidates of power resources, electrochemical energy storage (EES) devices have drawn more and more attention due to their ease of use, environmental friendliness, and high transformation efficiency. The performances of EES devices, such as lithium-ion batteries, sodium-ion batteries, and supercapacitors, depend largely on the inherent properties of electrode materials. On account of the outstanding properties of graphene, a lot of studies have been carried out on two-dimensional (2D) materials. Over the past few years, a new exfoliation method has been utilized to successfully prepare a new family of 2D transition metal carbides, nitrides, and carbonitrides, termed MXene, from layered precursors. Moreover, some unique EES properties of MXene have been discovered. With rapid research progress on this field, a timely account about the applications of MXene in the EES fields is highly necessary. In this article, the research progress on the preparation, electrochemical performance, and mechanism analysis of MXene is summarized and discussed. We also propose some personal prospects for the further development of this field.

1. Introduction

Along with economic development, the problems of energy shortage and environmental pollution have become more and more serious over the world. Thus, green power sources are necessary to satisfy future energy requirements [1–3]. Renewable energy sources, such as tidal power, wind power, and solar power, have been successfully developed [4,5]. However, these sources are intermittent. Accordingly, reliable and efficient energy storage techniques are being widely investigated [6–9]. Electrochemical energy storage (EES), such as Li-ion batteries (LIBs) [10–12], Na-ion batteries (NIBs) [13,14], Li-sulfur (Li-S) batteries [15,16], and supercapacitors (SCs) [17–19], are becoming most promising candidates of power resources due to their ease of use, environmental friendliness, and high transformation efficiency [20–22]. Vast amounts of research have focused on enhancing the performance of these energy storage devices [23–26]. Of all the factors have been analyzed, electrode materials play the most important role in improving their performance [27–30].

Since graphene has been discovered and developed [31–33], researches on two-dimensional (2D) materials and their characteristics have attracted extensive attention in the field of materials science [34]. Recently, 2D transition metal carbides, nitrides, and carbonitrides (referred to as MXenes) have developed rapidly since the discovery of Ti_3C_2 in 2011 [35]. MXenes are prepared by selective etching of certain atomic layers from their layered precursors, as known as MAX phase [36–38]. The MAX phases have a general formula of $M_{n+1}AX_n$ (n = 1, 2, 3), where M represents early transition metals (M = Ti, Sr, V, Cr, Ta, Nb, Zr, Mo, or Hf), A represents main-group sp elements (mostly IIIA or IVA), and X represents either C or N as well as both [39,40]. It can be described that MAX phase is the inter-growth structures with close-packed planar A atomic layers and alternative stacking of hexagonal MX layers. Fig. 1 presents classical configurations of MAX systems (taking Ti_2AlC as an example). In this structure, the M–X bond is mainly an assortment of ionic/covalent characteristics, while the M–A bond is purely metallic [41]. Therefore, the M–X bond is stronger than the M–A bond, which makes it possible to extract A layer from the layered solid. Nevertheless, different from weak Van der Waals' force interlayer interaction with graphite and transition metal di-chalcogenides, the M–A bond strengths are relative strong, which makes the separation of MX layers from MAX phases cannot be realized easily with direct dispersion or mechanical cleavage as well as ultrasonication. Due to the different characteristics and strengths between M–X and M–A bonds, the A layer with a relative high reactivity can be selectively etched by using suitable chemical(s). And the chemically more stable closely packed

Peer review under responsibility of Chinese Materials Research Society.

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https://doi.org/10.1016/j.pnsc.2018.03.003
Received 17 January 2018; Accepted 16 February 2018

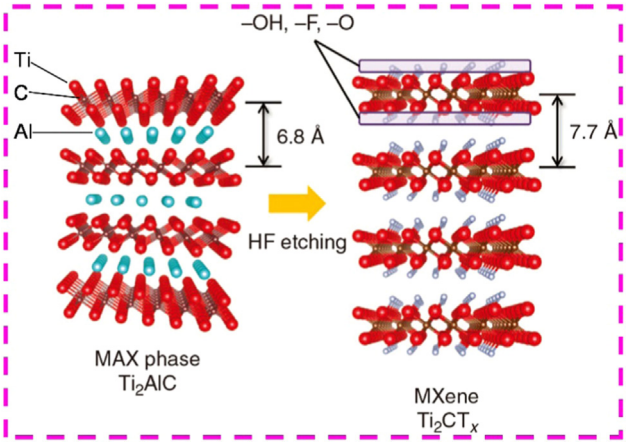

Fig. 1. Schematic illustration for the formation of Ti_2CT_x MXene from Ti_2AlC phase. a) Reproduced with permission [41]. Copyright 2015, Nature.

$M_{n+1}X_nT_x$ (T stands for surface-terminating functional groups like -F, -OH, -O) layers, namely MXene, are left (Fig. 1). The interactions between the layers of MXene are mainly hydrogen bonding and van der Waals bonding. Water, cations, DMSO, TBAOH, and so on, can be intercalated of into the interlayer spacing of MXene. Followed by sonication treatment, it is possible to delaminate MXenes to produce single-flake suspensions.

MXenes not only have 2D lamellar structure but also possess surface hydrophilic property and good electric conductivity [42]. Furthermore, they can host many different cations between their layers [43]. These exceptional properties have attracted wide attention from various fields, such as energy storage, catalysis, adsorption, sensor, and hydrogen storage. Up to now, applications of MXenes in EES have attracted the most interest [44–46]. MXene-based materials with varied chemistry properties and structures showed competitive performance [47]. Herein, we give a review about MXenes used in EES, including LIBs, NIBs, SCs, and Li-S batteries. First, we introduce the synthesis method of MXenes. Then, some typical applications are presented and discussed. Finally, existing problems and future trends are discussed.

2. Preparation

MXene materials are usually prepared by selective etching of weakly bonded A layers at room temperature in their homologous MAX phases, such as using HF solution [48]. According to pioneering experiment [35], $Ti_3C_2T_x$ was prepared by extracting Al layers from Ti_3AlC_2 phase. The reactions of HF solutions with Ti_3AlC_2 are depicted as follows:

$$Ti_3AlC_2 + 3HF = AlF_3 + 3/2H_2 + Ti_3C_2 \quad (1)$$

$$Ti_3C_2 + 2H_2O = Ti_3C_2(OH)_2 + H_2 \quad (2)$$

$$Ti_3C_2 + 2HF = Ti_3C_2F_2 + H_2 \quad (3)$$

Reaction (2) and Reaction (3) give rise to the formation of -OH and -F terminations, respectively. The solids were later separated through centrifugation and were then washed with H_2O. Before delamination, MXenes have multilayered structures. The sample was then performed by sonication and by intercalation of DMSO (dimethyl sulfoxide), to obtain single- or few-layer MXenes [49].

This method can be used to prepare nearly all kinds of MXene sheets from Al-containing MAX phases. The etching situations (time and HF concentration) depend on the size of MAX particle and reaction temperature [50]. For example, reducing the particle size of MAX phase through attrition or ball milling way can decrease the etching time and/or HF concentration effectively [51,52]. Beyond that, differences in M–Al bond energies also require diverse etching conditions for different MAX phases [51,53]. As a consequence, appropriate etching conditions are key factors of achieving high production and completing the conversion from MAX to MXenes.

In 2014, Halim et al. reported the use of NH_4HF_2, which functions as an etchant instead of the hazardous HF, to prepare MXenes [54]. This method is more suitable to prepare MXenes because of its milder nature and concomitant intercalation of cations during the etching process. While etching and intercalation processes occur at the same time, it is concluded that the following reactions occur in some cases:

$$Ti_3AlC_2 + 3NH_4HF_2 = (NH_4)_3AlF_6 + 3/2H_2 + Ti_3C_2 \quad (4)$$

$$Ti_3C_2 + aNH_4HF_2 + bH_2O = (NH_3)_c\,(NH_4)_dTi_3C_2(OH)_xF_y \quad (5)$$

The atomic layers in $Ti_3C_2T_x$ are more congruously spaced and appear to be conglutinant due to slower and less vigorous reaction processes, as well as the intercalation of both NH_3 and NH_4^+.

Ghidiu et al. reported a high-yield approach for the preparation of MXene sheets [55]. $Ti_3C_2T_x$ was prepared by dissolving Ti_3AlC_2 powders in aqueous solution of LiF and HCl. Then the mixture was heated at 40 °C for 45 h. After washing the sediment, the product was obtained. A clay-like paste was formed during this process, which could be rolled to prepare flexible and free-standing films. The resultant flakes possess larger lateral dimensions without nanoscale defects, which are observed frequently in HF-etched samples [56]. Intriguingly, fluoride salts and acids in other combinations, such as KF, NaF, CsF, tetrabutylammonium fluoride [$(C_4H_9)_4NF$], and CaF_2 with H_2SO_4 or HCl, showed similarities among etching behaviors. This milder etching approach plays a heuristic role in future explorations.

3. Applications

3.1. Li-ion batteries (LIBs)

LIBs have been widely used in the field of portable electric devices due to their high energy density and good cycling performance. To further improve the performance of LIBs, it is of great importance to develop new electrode materials.

3.1.1. Simplex MXene

Not long after the discovery of MXene materials, the possibility of using MXene as LIBs anode materials was studied [35,57]. For example, Xie et al. predicted the theoretical capacity of 320 mA h g^{-1} for Li intercalation of bare Ti_3C_2 [58]. However, the presence of –F or –OH on MXene surface, limits the storage capacity for Li^+. In reality, Tang et al. reported that the capacity was only about 130 mA h g^{-1} for $Ti_3C_2F_2$ and 67 mA h g^{-1} for $Ti_3C_2(OH)_2$ [59]. As early as 2012, Ahmed et al. utilized the Ti_2C MXene treated with hydrogen peroxide (H_2O_2) as the anode material in LIBs [60]. The H_2O_2 treatment gives rise to open up MXene sheets and form TiO_2 nanocrystals on the surface of sheets. The H_2O_2 treated MXene showed an enhanced discharge specific capacity (389 mA h g^{-1} at 100 mA g^{-1} after 50 cycles) and better rate capability (150 mA h g^{-1} at 5 A g^{-1}) compared to pure Ti_2C MXenes. Mashtalir et al. fabricated a Ti_3C_2 'paper' in 2013 with the method of filtering the Ti_3C_2 colloidal solution followed by intercalating with DMSO and finally dispersing it by sonication [49]. The electrode possessed a capacity of 410 mA h g^{-1} at 1 C and maintained 110 mA h g^{-1} at 36 C after 700 cycles. The formation of extra Li layers on the already-lithiated O-terminated MXene may result in the increase of the capacity [61].

In addition to mostly reported titanium carbides MXene, other types of MXene materials have also attracted considerable attention [40,62–64]. For example, Naguib et al. reported the new 2D Nb_2C and V_2C (Fig. 2a and b) for LIBs [51]. The layered sample (Fig. 2c) was prepared by etching of Al atom from Nb_2AlC and V_2AlC at room temperature. Reversible capacities of 170 and 260 mA h g^{-1} at 1 C, and 110 and 125 mA h g^{-1} at 10 C were obtained after 150 cycles, respectively (Fig. 2d). These new materials demonstrated good cycling performance. Because of the complexity of the composition, Yu et al. explored the