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MXene: a promising transition metal carbide anode for lithium-ion batteries

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ABSTRACT

Herein we report on Li insertion into a new two-dimensional (2-D) layered Ti₂C-based material (MXene) with an oxidized surface, formed by etching Al from Ti₂AlC in HF at room temperature. Nitrogen sorption of treated powders showed desorption hysteresis consistent with the presence of slit-like pores. At 23 m² g⁻¹, the specific surface area was an order of magnitude higher than untreated Ti₂AlC. Cyclic voltammetry exhibited lithiation and delithiation peaks at 1.6 V and 2 V vs. Li⁺/Li, respectively. At C/25, the steady state capacity was 225 mAh g⁻¹; at 1C, it was 110 mAh g⁻¹ after 80 cycles; at 3C, it was 80 mAh g⁻¹ after 120 cycles; at 10C, it was 70 mAh g⁻¹ after 200 cycles. Since Ti₂C is a member of the MXene family – where M is an early transition metal and X is C and/or N – that to date includes Ti₃C₂, Ta₄C₃, TiNbC, and (V_{0.5}Cr_{0.5})₃C₂, our results suggest that MXenes are promising as anode materials for Li-ion batteries.

Keywords:

Lithium-ion batteries

Two-dimensional materials

Titanium carbide

MXene

Anode

1. Introduction

Li-ion batteries (LIB) are a key technology and play a dominant role in today's world, especially for transportation [1] and renewable energy storage [2]. Extensive research efforts have been dedicated to exploring and developing new anode materials for LIBs [3]. The goal of much of the research is to develop new materials with higher capacities and lifetimes than current graphite or lithium titanate anodes. With Si insertion anodes receiving much attention in the past few years [4,5], there is certainly a need to explore other materials.

Exfoliated materials with large specific surface areas, such as graphene [6] and MoS₂ [7], show promise as anodes in secondary LIBs, due to their large surface areas. While anodes based on titanium oxide (TiO₂) and lithium titanate (Li₄Ti₅O₁₂) exhibit lower specific capacities than graphite (LiC₆), they are still considered viable candidates due to their improved safety and high-rate performances [8–10].

Recently, a new family of exfoliated transition metal carbides and carbonitrides called “MXene” has been synthesized by wet HF treatment of Al-containing MAX phases [11,12]. The latter is a family (>60 members) of ternary early transition metal carbides, carbonitrides, and nitrides with a layered hexagonal structure (space group P6₃/mmc) and M_{n+1}AX_n chemistry, where “M” is an early transition metal, “A” is an A-group element (mostly groups 13 and 14), “X” is

carbon or nitrogen, and $n = 1, 2$, or 3 [13]. The structure is comprised of M₆C octahedra, interleaved with layers of A atoms. Immersing Al-containing MAX phases, such as Ti₃AlC₂, Ti₂AlC or V₂AlC, in HF solutions results in the Al being selectively etched away. The resulting M_{n+1}C_n layers are terminated with mostly oxygen and/or fluoride groups that are weakly bonded together, making them susceptible to exfoliation. DFT calculations also predict that changing the surface groups would lead to changes in the band gap of the MXenes [11]. The electric conductivities of freestanding, cold pressed MXene disks were found to be comparable to multi-layer graphene [12].

Ti₂AlC is one of the most common and cheapest MAX phases. Powders with particles smaller than 45 μm (– 325 mesh) are commercially available. Taking into account that it is also an excellent electronic conductor and its etching and exfoliation produces the lightest MXene, Ti₂C, we chose to explore its potential as an anode material. Herein we report, for the first time, on the electrochemical behavior and Li⁺ uptake of exfoliated Ti₂C.

2. Experiment

2.1. Synthesis of Exfoliated Ti₂C

Pre-reacted, – 325 mesh, Ti₂AlC powders were commercially obtained (3-ONE-2, Voorhees, NJ, >92 wt.% purity). The exfoliation process was carried by immersing the Ti₂AlC powder in diluted (10%) hydrofluoric acid, HF, (Fisher Scientific, Fair Lawn, NJ) for 10 h at room temperature, as described elsewhere [12].

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2.2. Characterization

A scanning electron microscope, SEM, (Zeiss Supra 50VP, Germany) equipped with an energy-dispersive spectrometer, EDS, (Oxford Inca X-Sight, Oxfordshire, UK) was used to obtain high magnification images of the treated powders and estimate the chemistry of the HF treated Ti_2AlC .

Gas sorption analysis was carried out using a Quantachrome Autosorb-1 with nitrogen, N_2 , adsorbate. Prior to the analysis, the samples were outgassed under vacuum at 200°C for 48 h. Nitrogen sorption analysis at 77 K was used for calculating the specific surface area (SSA) using the Brunauer–Emmet–Teller (BET) equation.

2.3. Electrochemical testing

To investigate the electrochemical behavior of exfoliated Ti_2AlC in Li batteries, coin cells (CR 2016) were assembled. The working electrodes were made with 80 wt.% Ti_2C (as described above) and 10 wt.% Super P carbon black mixed with 10 wt.% poly(vinylidene fluoride) dissolved in 1-methyl-2-pyrrolidinone. The mixture was then spread onto a copper foil and dried at $\approx 200^\circ\text{C}$ for 12 h, under a mechanical vacuum. CR 2016 coin-type cells were assembled using MXene as the positive electrode and Li metal foil as the negative electrode, separated by a sheet of borosilicate glass fiber (Whatman GF/A) separator saturated with 1 M LiPF_6 solution in a 1:1 weight mixture of ethylene carbonate and diethyl carbonate (EC:DEC) as the electrolyte. The cells were assembled inside an Ar-filled glove box with H_2O and O_2 contents < 1 ppm, to avoid any moisture contamination.

The cells were subjected to cyclic voltammetry and galvanostatic charge–discharge cycling using a potentiostat (VMP4, Biologic, S.A.). Electrochemical characterization was typically performed between 0.05 V and 2.5 V vs. Li^+/Li .

3. Results and discussions

X-ray diffraction, XRD, of the reacted powders indicated that the Al was selectively etched from the structure [12]. EDS confirmed that the Al layers were replaced by O and F. The presence of the latter was explained by assuming that the Ti-surfaces, exposed by the removal of the Al, were terminated by oxygen and possibly fluoride surface groups [12]. SEM images of Ti_2AlC particles after HF treatment (Fig. 1a) resemble images of exfoliated graphite and clearly show HF-induced delamination that is typical of MXenes [11,12].

The N_2 sorption isotherm of the treated powders (Fig. 1b) has a hysteresis loop with indications of the presence of mesopores and a shape typical for slit pores [14]. The SSA calculated using the BET equation [15] for the HF treated Ti_2AlC was $23\text{ m}^2\text{ g}^{-1}$. This value is about an order of magnitude higher than the as-received Ti_2AlC powders measured at $\approx 2.5\text{ m}^2\text{ g}^{-1}$.

Typical cyclic voltammetry curves, at a rate of 0.2 mV s^{-1} , for the exfoliated Ti_2C are shown in Fig. 2a. A broad, irreversible peak was observed around 0.6 V, during the first lithiation cycle (reduction); it was absent in subsequent cycles. It is reasonable to preliminarily assign this irreversible peak to the formation of a solid electrolyte interphase (SEI) and to an irreversible reaction with the electrode material. In all subsequent cycles, broad reversible peaks were observed at 1.6 V and 2.0 V vs. Li^+/Li during lithiation and delithiation, respectively. Because these peak potentials are similar to those reported for TiO_2 and lithiated titania [9] we tentatively assign these peaks to the following redox reaction:



The rationale for this assignment is that drying at 200°C , prior to assembling the coin cells, rids the MXene of water or any OH species

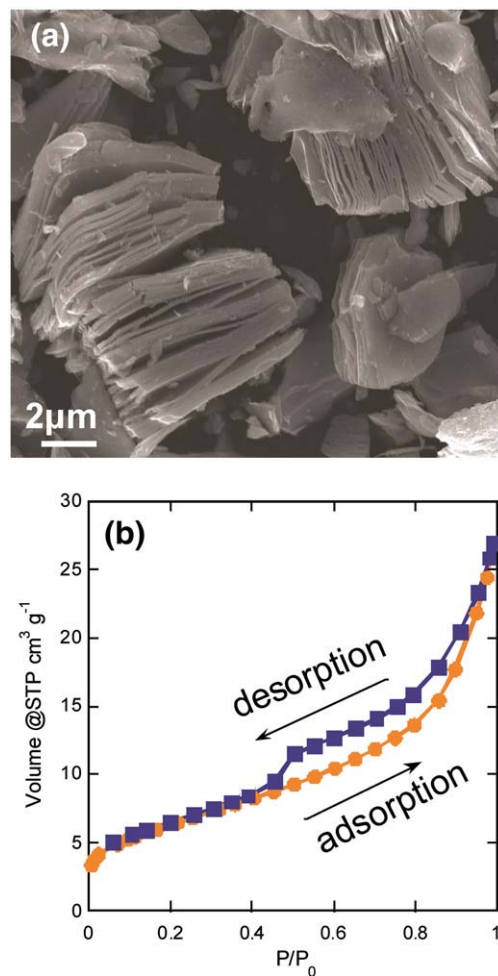


Fig. 1. (a) SEM image of exfoliated Ti_2CO_x produced by HF treatment of Ti_2AlC ; (b) N_2 adsorption–desorption isotherms of the material shown in (a), orange circles refer to adsorption and blue squares refer to desorption. The calculated SSA is approximately $23\text{ m}^2\text{ g}^{-1}$.

and leads to an oxygen terminated surface [16]. In other words: the assumption is made that the Ti_2CO_x surface is similar to that of titania. Like in the case of the titanates, even if the potentials vs. Li are relatively high, it is an advantage from a safety stand point [17]. *Ex situ* XRD results (not shown) after lithiation produced no new peaks, but a downshift of the MXene peaks was observed, with an increase of the *c* parameter by 19.5% which indicates intercalation of Li between the MXene layers, and not a conversion reaction.

Fig. 2b shows the galvanostatic charge/discharge curves at a rate of C/10 (1 Li^+ per formulae exchanged in 10 h). The capacity loss in the first cycle can again be attributed to a SEI layer formation at potentials below 0.9 V vs. Li^+/Li [18], as well as to the irreversible reduction of electrochemically active surface groups such as fluorine or possibly hydroxyls. The specific capacity stabilized after five cycles at $\approx 160\text{ mAh g}^{-1}$. This value corresponds to $y \approx 0.75$ in reaction (1).

At 160 mAh g^{-1} , the capacity of the treated powders is about 5 times higher than that of the as-received Ti_2AlC ($\approx 30\text{ mAh g}^{-1}$ at C/10) powders. This increase in capacity is traceable to the higher surface area, more open structure and weaker bonds between the MX layers after HF treatment. In addition to the morphological changes, the Li insertion sites are also now different (i.e., the site binding energies) which could also explain the differences in capacity.

The specific capacities vs. cycle number at different cycling rates (C/25, C/6, 1C, 3C, and 10C) calculated from galvanostatic curves are shown in Fig. 2c. The highest capacity was obtained at a rate of

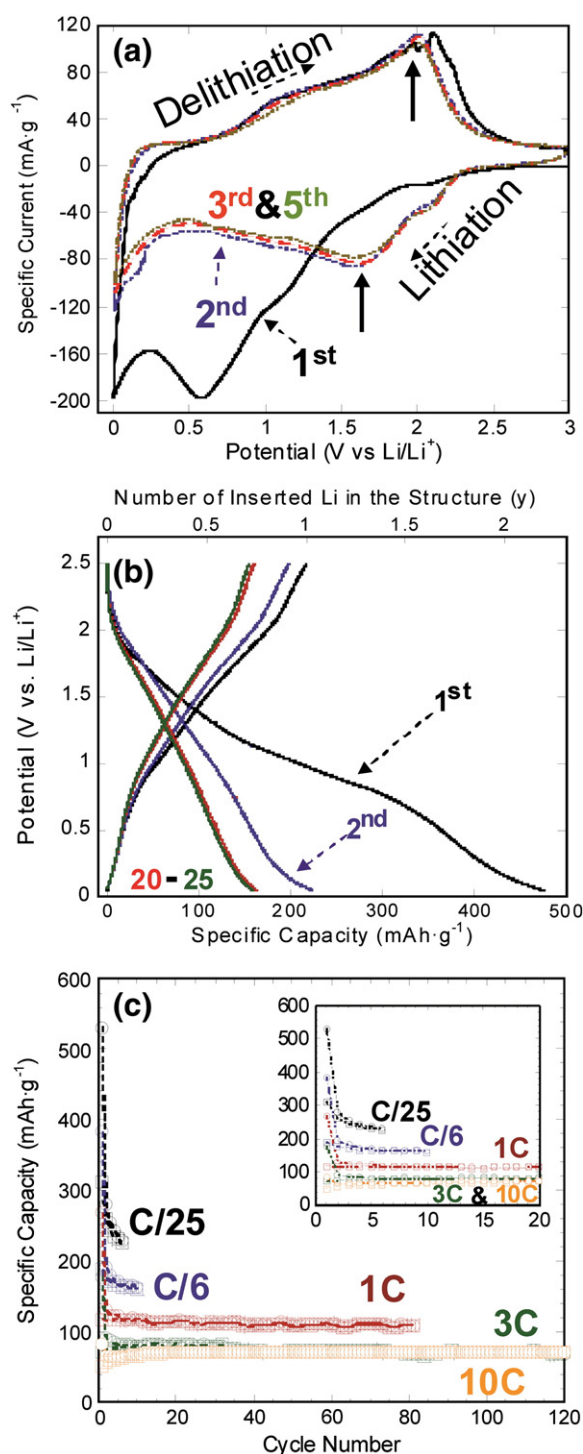


Fig. 2. (a) Cyclic voltammetry curves of exfoliated Ti_2C at a constant scan rate of 0.2 mV s^{-1} . The solid arrows refer to main peaks positions during lithiation and delithiation cycles. (b) The galvanostatic charge/discharge curves at a C/10 rate. (c) Specific lithiation (circles in the figure) and delithiation (squares in the figure) capacities (per mass of active material) vs. cycle number at different rates. The inset in Fig. 2c is a zoom of the first 20 cycles.

C/25. The specific capacity values stabilize after 5 cycles, for all scan rates. At a C/25 rate, the capacity is 225 mAh g^{-1} , which corresponds to $y \approx 1$. At rates of 1C and 3C, the capacities, after 80 cycles, were, respectively, 110 mAh g^{-1} and 80 mAh g^{-1} . Even at rates of 10C, a stable capacity of 70 mAh g^{-1} was obtained for more than 200 cycles. These results clearly demonstrate that it is possible to electrochemically

intercalate Li^+ ions in the interlayer spaces between exfoliated Ti_2C sheets, and achieve stability.

These results, while not yet at the level of thoroughly studied and optimized titanate anodes that have similar Ti–O surface chemistries [9,19–21], are to be considered promising when compared to any currently used anode materials, including graphite or titania – based anodes, at comparable – i.e., first report – stages of development. It is reasonable to assume that with further work on these new materials significant improvement will be made. Fruitful research avenues include optimizing the grain size of the original MAX phases as was reported for other systems [22–25], and/or tuning the MXene compositions [26–28].

With more than 60 MAX phases known, this study opens the door to exploring a large family of promising electrode materials. It is worth noting here that we have already exfoliated Ti_3C_2 , Ta_4C_3 , TiNbC , and $(\text{V}_{0.5}\text{Cr}_{0.5})_3\text{C}_2$ [12], and are currently exploring their potential as Li anodes.

4. Conclusions

In conclusion, exfoliated Ti_2C , produced by HF treatment of Ti_2AlC powders, showed reversible capacity about 5 times higher than pristine Ti_2AlC , due to its open structure, weaker interlaminar forces, and higher SSA. Electrochemical measurements showed intercalation and deintercalation of Li^+ ions at 1.6 V and 2 V vs. Li^+/Li , respectively. The exfoliated Ti_2C material exhibited a stable capacity of 225 mAh g^{-1} at a C/25 rate, corresponding to about one Li per Ti_2CO_x formula unit. A stable cycling capacity of 80 mAh g^{-1} was observed after 120 cycles at a 3C rate, and 70 mAh g^{-1} was observed after 200 cycles at a 10C rate. These results are encouraging and suggest that the MXenes could be used as Li^+ intercalation electrodes in LIBs.

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