Original Article

The preparation of V$_2$CT$_x$ by facile hydrothermal-assisted etching processing and its performance in lithium-ion battery

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ABSTRACT

In this study, high-purity V$_2$CT$_x$ MXene was successfully synthesized by etching V$_2$AlC with fluoride and hydrochloric acid mixed solution using a hydrothermal-assisted method. This method is more concise and effective and has a low level of danger. The morphology and structure of the V$_2$CT$_x$ MXene was characterized by X-ray diffraction, field emission scanning electron microscopy, and X-ray photoelectron spectroscopy. The electrochemical properties were investigated as an anode material for lithium ion batteries. The results show that the prepared V$_2$CT$_x$ had a higher purity and showed excellent electrochemical properties as an anode of lithium-ion batteries. And V$_2$CT$_x$ prepared with different etching system can be obtained with high yield and excellent purity by changing the reactive conditions of the system. However, electrochemical performance of V$_2$CT$_x$ MXene obtained at different etching system is quite different. V$_2$CT$_x$ synthesized in the mixed solution of ammonium fluoride and hydrochloric acid has the best performance, which originates from more accessible active sites for ion in the enlarged interlayer distance, and the smaller impedance of V$_2$CT$_x$.

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1. Introduction

MXenes are a new type of 2D transition metal carbides and/or nitrides nanomaterials, which was firstly synthesized by selective etching of the Al element layers from MAX phase Ti$_3$AlC$_2$ with hydrofluoric acid (HF) in 2011 by Naguib et al. [1]. Generally, a MXene is synthesized by exfoliating MAX phases with hydrofluoric acid, which is not safe or environmentally friendly. Therefore, the method for MXene synthesis using the solution of fluoride salt and hydrochloric acid has been developed. As the precursor of MXene, MAX phase has a chemical general formula of M$_{n+1}$AX$_n$ (n = 1,2,3…), where M is an early transition metal element, A belongs to the main groups III/IV elements, and X represents C or/and N elements [2,3]. The diversity of MAX gives the designability of composition and structure of MXene, such as Ti$_3$C$_2$ [1,4], Ti$_2$C$_2$ [5,6], V$_2$C [7], Nb$_2$C [8], Mo$_2$C [9,10], Ti$_2$CN [4,11], Nb$_2$C$_2$ [12], (Ti$_{0.5}$Nb$_{0.5}$)$_2$C [4], and (V$_{0.5}$Cr$_{0.5}$)$_2$C$_2$ [4]. A large amount of theoretical calculations and experiments indicate that MXenes have many excellent

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physical and chemical properties and were widely used in many fields such as adsorption materials [13–15], catalytic materials [16–19], polymer reinforced materials [20–22], lubricant additives [23,24], and especially energy storage materials [25–29].

Among the MXene materials, V$_2$CT$_x$ have a better performance than many other MXenes and has attracted great attention due to its novel properties. Theoretical analysis indicates that V$_2$CT$_x$ MXene is a promising material as a highly active catalyst for hydrogen evolution reaction [30], uranium capture materials for nuclear waste treatment [31,32], hybrid material for the CO$_2$ and temperature responsive [33] and an energy storage material for batteries [7,34]. Naguib et al. [35] and Sun et al. [36] found that V$_2$CT$_x$ MXene is an ideal material for Li ion batteries (LIBs) with the theoretical capacity of up to 940 mA h g$^{-1}$, which is much higher than that of Nb$_2$C and Ti$_2$C.

Up until now, the main method of preparing V$_2$CT$_x$ is to etch V$_2$AlC in HF solution or in the mixed solution of fluoride salts and hydrochloric acid. However, because of the high formation energies of V$_2$C from V$_2$AlC [27], the complete exfoliation of V$_2$AlC is difficult, and the obtained V$_2$CT$_x$ tends to contain a certain amount of unreacted V$_2$AlC. Therefore, the transformation efficiency of V$_2$AlC into V$_2$C are still to be improved, which is of great importance for the further applications of V$_2$CT$_x$ MXene.

In this paper, based on the previous studies of our work [7,37], the highly pure V$_2$CT$_x$ MXene was successfully prepared by a simple hydrothermal-assisted method. Effects of the reactants, temperature and time on the yield of the product were studied in details. Meanwhile, the electrochemical performance as an anode for LIBs were also investigated. This method for MXene V$_2$CT$_x$ synthesis has moderate reaction conditions and is much safer, easier and more efficient compared with other methods.

2. Experimental

2.1. Sample preparation

V$_2$AlC powders were pre-made by a tube furnace in Ar atmosphere and passed in 500 mesh sieves [38]. In a typical synthesis, 2 g V$_2$AlC powders were added into 40 mL mixed solution of 0.05 mol lithium fluoride (sodium fluoride, potassium fluoride and ammonium fluoride) and 40 mL hydrochloric acid (6 M) by magnetic stirring. The reaction mixture was sealed in a Teflon-lined stainless-steel autoclave with 100 mL capacity, kept at 90 $^\circ$C for 5 days, and then allowed to cool to room temperature naturally. Black precipitates were centrifugally collected and washed several times by deionized water and absolute ethanol. Finally, the precipitates were dried under vacuum at 60 $^\circ$C for 12 h. The samples obtained with lithium fluoride, sodium fluoride, potassium fluoride and ammonium fluoride were named V$_2$CT$_x$-Li, V$_2$CT$_x$-Na, V$_2$CT$_x$-K and V$_2$CT$_x$-N. To understand the influence of temperature (60, 90 and 120 $^\circ$C) and time (3, 5 and 7 days) on the exfoliating process, more experiments were carried out in the same reaction system.

2.2. Measurements and observations

X-ray diffraction (XRD) pattern was obtained by D8 Advance Bruker X-Ray diffractometer equipment with Cu K$_\alpha$ radiation. The sample was scanned over the range (2θ) 5–80 $^\circ$ with a scanning rate of 15’ min$^{-1}$ to identify the crys-

![Fig. 1 - The XRD patterns of V$_2$CT$_x$ synthesized by etching V$_2$AlC with (a) LiF, (b) NaF, (c) KF and (d) NH$_4$F in different time at 90 $^\circ$.](image-url)
The morphology and microstructures of the samples were examined using a field emission scanning electron microscopy (FESEM, Merlin Compact, Carl Zeiss NTS, acceleration voltage = 15 kV) with energy-dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM, JEOL JEM-2010, Japan, acceleration voltage = 100 kV). X-ray photoelectron spectroscopy (XPS) analysis was carried out to reveal the chemical state of the elements of V₂CTₓ MXene surface on PHI-5702 multifunctional X-ray photoelectron spectrometer, Mg Kα radiation was used as an exciting source, using the binding energy of contaminated carbon (C1s: 284.8 eV) as reference.

### 2.3. Electrochemical characterization

The electrochemical tests were carried out in a standard CR2016 coin cell. The anode electrodes were prepared by mixing the active material, Super P, and a polyvinylidene fluoride (PVDF) binder in a mass ratio of 8:1:1 in a solution of N-methyl-2-pyrrolidinone (NMP) and stirred for several minutes. The resulting slurry was then pasted on a Cu foil and dried in a vacuum oven at 110°C for 12 h. The battery was assembled in an argon-filled glove box (H₂O<1 ppm, O₂<1ppm) using lithium metal as the counter electrode. The electrolyte was 1 M LiPF₆ in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethylmethyl carbonate (EMC) in a 1:1:1 volume ratio. The coin cells were tested on a XINWEI workstation, with a current density ranging from 50 mA g⁻¹ to 1000 mA g⁻¹ with a voltage range from 0.01–3.0 V. Cyclic voltammetry (CV) measurements were performed on an EQCM440 workstation (Shanghai Chenhua, China) at a scan rate of 0.2 mVs⁻¹. Electrochemical impedance spectroscopy (EIS) was measured on an electrochemical workstation (Parstat 2273, Princeton) with a frequency range from 50 mHz to 100 kHz.

### 3. Results and discussion

The influence of fluoride salts has an important effect on the etching process. The XRD patterns of V₂CTₓ synthesized by etching V₂AlC with different fluoride salt and time are shown in Fig. 1. The diffraction peaks with 2θ values at 13.5, 35.6, 36.2, 39.0, 41.3 and 55.5° correspond to the crystal plane (002), (100), (101), (103), and (106) of crystalline V₂AlC, respectively (PDF 29-0101). After the etching of V₂AlC with different mixture solution of fluorine salt and hydrochloric acid, the characteristic diffraction peaks of V₂AlC disappeared gradually and the characteristic diffraction peaks of V₂CTₓ appeared with the

<table>
<thead>
<tr>
<th>3 days</th>
<th>5 days</th>
<th>7 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiF</td>
<td>– 2µm</td>
<td>– 2µm</td>
</tr>
<tr>
<td>NaF</td>
<td>– 2µm</td>
<td>– 2µm</td>
</tr>
<tr>
<td>KF</td>
<td>– 2µm</td>
<td>– 2µm</td>
</tr>
<tr>
<td>NH₄F</td>
<td>– 2µm</td>
<td>– 2µm</td>
</tr>
</tbody>
</table>

Fig. 2 – FESEM images of V₂CTₓ prepared with four mixture solution in different time at 90°C.
reaction time extending. The characteristic diffraction peak with 2θ about 7.4° can be assigned to the (002) plane of MXene V_{2}CT_{x} [7,30]. From Fig. 1, it can be found that the reaction system of NaF and HCl mixture solution has the fastest etching rate than other system, the V_{2}AlC precursor have almost been etched in three days. While the reaction system of KF has the slowest etching rate, which needs seven days. In addition, the position of characteristic diffraction peaks of V_{2}CT_{x} of alkali system (LiF, NaF and KF) are almost identical. However, the diffraction peak of V_{2}CT_{x} prepared with NH_{4}F has significantly shifted to a small angle. The enlarged interlayer distance means more accessible active sites for ion in the interlayer space, which will greatly enhance the performance of V_{2}CT_{x} materials in energy storage devices [39].

Fig. 2 is the FESEM images of V_{2}CT_{x} prepared with four mixture solution of LiF, NaF, KF, and NH_{4}F with HCl in different time at a temperature of 90 °C. As shown in Fig. 2, it can be observed that the reaction is very weak in a short time of three days. Indeed, the changing of the surface morphology is weak, especially for the V_{2}AlC etched at KF and HCl mixture solution. With the increase of the reaction time, HF produced by the fluoride salts and hydrochloric acid increased and impel the etching process of V_{2}AlC to become significant and quasi-2D MXene sheets were obtained. Hence, from the figure, it can be seen that the V_{2}AlC in different mixture solution are almost exfoliated into the layered structure.

To understand the influence of temperature on the exfoliating process, more experiments were carried out. Fig. 3 shows the XRD patterns of the samples exfoliated with different temperature. From the XRD patterns, it can be seen that the etching reaction was very weak at low temperature of 60°, and the etching efficiency is very low. The intensity of diffraction peaks of V_{2}AlC is still strong, only a very weak diffraction peak of V_{2}CT_{x} appeared. When the temperature increased to 90°, V_{2}CT_{x} peaks appeared obviously and the diffraction peaks of V_{2}AlC almost disappeared, with the exception of V_{2}AlC etched at KF and HCl mixture solution, which means most V_{2}AlC were exfoliated to V_{2}CT_{x}. If the reaction temperature was increased to 120°, the V_{2}AlC peaks all disappeared. The characterization shows that the width of XRD diffraction peak of V_{2}CT_{x} gets broader, and the diffraction peak of V_{2}CT_{x} significantly shifts to a smaller angle, meaning the enlarging of interplanar crystal spacing. However, something unknown was observed in the position of 2θ about 25°, which may be the residual aluminum fluoride or hydroxide crystals that cannot be easily washed off.

Fig. 4 is the FESEM images of V_{2}CT_{x} samples prepared at different temperatures for five days. It was found that temperature has a direct effect on the etching process. In the low temperature of 60°, lots of V_{2}AlC was still in its original form, especially in the mixture of KF and HCl system, which means the etching reaction was difficult to happen. With etching temperature increasing from 60 to 90 and/or 120°, it was observed that V_{2}CT_{x} MXene stacks become more separated. This illustrates that HF is easier penetrate into the layer and selectively etching the Al-layer in V_{2}AlC, and V_{2}CT_{x} is finally generated.

In order to obtain the surface information of V_{2}CT_{x} prepared with different fluoride salt, XPS analysis were carried
out and the results are shown in Fig. 5 and the surface atomic concentration of samples are shown in Table 1. XPS shows that the main composition of these samples are V, C, O, F, and Cl. Because of adventitious carbon always co-existing with MXene, this results in higher C concentration being detected by XPS. Chlorine element on the surface of V2CTx comes from the absorption of chloridion, while the Al element in the system of NH4F and HCl may be coming from the tiny amounts of aluminum salt residue. Interestingly, it was found that the atomic concentration of fluoride salt ions has a large difference on the surface of V2CTx. Li-ion has the maximum capacity, while K-ion has zero atomic concentration and Na-ion concentration is in the middle. This phenomenon shows that Li-ion is easier embedded in V2CTx than Na-ion and K-ion, which may be due to the minimum ionic radius. In addition, nitrogen element was also found on the surface of V2CTx, which means that NH4+ had intercalated into the layers of V2CTx. This led to an increase of d-spacing and reducing the Van der Waals force of V2CTx layers, which will contribute to exfoliate V2CTx into a single layer [40].

To better understand the chemical states of the V elements on the surface of V2CTx, deconvolution of the V2p region of the high resolution XPS spectra of V2CTx obtained with different fluoride salts are shown in Fig. 6. Deconvolution of the V2p region reveals the presence of V2+ (~513.5 eV), V3+ (~514.6 eV) and V4+ (~516.6 eV). The peaks at ~513.3 eV and ~521.1 eV (V2+) correspond to the incomplete etching of V2AlC MAX phase in the produced V2CTx MXene, as reported in previous studies. [41–43] The peaks around ~514.6 eV (V3+) ~516.7 eV (V4+) and ~524.1 eV (V4+) are attributed to the existence of a monolayer oxide/vanadium oxide mixture on the surface of V2CTx MXene nanosheets. [35,42] From the high resolution XPS spectra of V2p, it can be found that the relative intensity of the V2+ peaks of V2CTx obtained with NH4F is weakest, which means that the method with NH4F has a highest yield of V2CTx and a minimum residual amount of incomplete etched V2AlC MAX phase.

The charge-discharge profiles of different V2CTx samples as the LIBs anode, at different cycles with a current density...
Fig. 5 – XPS spectra of V$_2$CT$_x$ prepared by different mixture solution for 5d.

Fig. 6 – The high resolution XPS spectra of V2p of V$_2$CT$_x$. (a) LiF, (b) NaF, (c) KF, (d) NH4F.

of 50 mA/g in the voltage range from 0.01–3.0 V are shown in Fig. 7, respectively. The first discharge capacities of V$_2$CT$_x$-Li, V$_2$CT$_x$-Na, V$_2$CT$_x$-K and V$_2$CT$_x$-N are 1123.3, 613.6, 574.1, and 943.6 mAhg$^{-1}$, respectively, and the first charge capacities are 675.3, 373.4, 350.0, and 719.0 mAhg$^{-1}$, respectively. The first charge and discharge coulombic efficiencies of V$_2$CT$_x$-Li, V$_2$CT$_x$-Na, V$_2$CT$_x$-K and V$_2$CT$_x$-N are 60, 61, 61, and 76%, respectively. The low efficiency in the first cycle was mainly because of the formation of the SEI on the surface. Among them, V$_2$CT$_x$-N has maximum coulombic efficiencies.
Fig. 7 – Charge–discharge profiles of different $V_2CT_x$ electrode at different cycles with a current density of 50 mA/g.

**Table 2 – Electrochemical performance of $V_2CT_x$ and similar materials in other literature.**

<table>
<thead>
<tr>
<th>Materials</th>
<th>Method</th>
<th>1st discharge mAh/g</th>
<th>Cycling performance-discharge Capacity (nth) mAh/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-Nb$_2$CT$_x$</td>
<td>Nitrogen-doped</td>
<td>380 at 0.2C</td>
<td>360 (100th) at 0.2C</td>
</tr>
<tr>
<td>$V_2CT_x$</td>
<td>HCl + NaF-etching</td>
<td>467 at 50 mA/g</td>
<td>243 (500th) at 50 mA/g</td>
</tr>
<tr>
<td>$V_2C_2Tx$-HF</td>
<td>HF-etching</td>
<td>164.1 at 100 mA/g</td>
<td>125 (300th) at 100 mA/g</td>
</tr>
<tr>
<td>Ti$_2$Cl$_2$-Ti$_2$O$_2$</td>
<td>Freeze-drying</td>
<td>367 at 200 mA/g</td>
<td>267 (500th) at 200 mA/g</td>
</tr>
<tr>
<td>Nb$_4$C$_2$Tx</td>
<td>HF-etching</td>
<td>231.4 at 100 mA/g</td>
<td>69 (100th) at 100 mA/g</td>
</tr>
<tr>
<td>Mo$_2$CT$_x$</td>
<td>HCl + LiF-etching</td>
<td>323 at 50 mA/g</td>
<td>274.85 (300th) at 50 mA/g</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx</td>
<td>HF-etching</td>
<td>335.5 at 50 mA/g</td>
<td>70 (1000th) at 1000 mA/g</td>
</tr>
<tr>
<td>rGO</td>
<td>Freeze-dried</td>
<td>267 at 66.7 mA/g</td>
<td>208.26 (1000th) at 66.7 mA/g</td>
</tr>
<tr>
<td>$V_2CT_x$-N</td>
<td>Hydrothermal etching</td>
<td>943.6 at 50 mA/g</td>
<td>233 (50th) at 1000 mA/g</td>
</tr>
</tbody>
</table>

Fig. 8(a–d) shows the typical cyclic voltammetry (CV) plots of lithium storage behavior of the different $V_2CT_x$ electrodes, with an electrochemical window of 3.0 V–0.01 V at a scan rate of 0.2 mV s$^{-1}$. As shown in Fig. 8a–d, the CV curve shape of $V_2CT_x$ is similar to that reported in the literature [44]. Cyclic voltammetry curves of $V_2CT_x$ do not exhibit a distinct reduction peak. The main weakly reduction peak of the $V_2CT_x$ electrode is about 1.1 V in the first lithiation process, and then disappears in the following Li-ion intercalation process. This could mainly be due to the formation of SEI companion on the electrode surface to trapping of Li$^+$ on the sheets of $V_2CT_x$ [45]. In the cycle for the oxidation process, a peak at about 2.0 V maybe caused by Li ion extraction from the $V_2CT_x$ layers. The cycling performances of MXene $V_2CT_x$ samples electrodes at different current densities were tested, and the results are shown in Fig. 8e. In the first ten cycles at a current density of 50 mA g$^{-1}$, the capacities of all four electrodes were unstable, and this was due to the formation of the SEI film [46]. From the first 60 cycles, it can be seen that the $V_2CT_x$-N electrode has a high capacity at a different rate and that the capacity has no obvious attenuation. In the latter 50 cycles, when the current density was reduced back to 1000 mA g$^{-1}$, the cell maintained a stable capacity, and the efficiency remained at almost 100%. In all of the cycles, $V_2CT_x$-N had a higher time capacity than $V_2CT_x$-Li, $V_2CT_x$-Na, and $V_2CT_x$-K. The increase of the capacity of $V_2CT_x$-N materials in LIBs may be due to the enlarged interlayer distance (as shown in XRD and SEM), which can provide more accessible active sites for ion in the interlayer space. By contrast, the electrochemical results of $V_2CT_x$-N are better than other similar materials in some previous reports in Table 2.

Fig. 8f is the electrochemical impedance spectroscopy of the $V_2CT_x$ electrodes. From the spectroscopy, it can be found that $V_2CT_x$ obtained from NH$_4$F and HCl etching system has
Fig. 8 – Characterization of Li-ion batteries made using different V$_2$CT$_x$ anodes, including (a–d) Cyclic voltammetry curves, (e) Rate performance and (f) Electrochemical impedance spectroscopy Nyquist plots.

the smallest semicircular diameter in the high frequency region, meaning a better charge transfer efficiency in the four electrodes [47]. Moreover, V$_2$CT$_x$-Li, V$_2$CT$_x$-Na and V$_2$CT$_x$-K had the highest impedances. The straight line in the low frequency region was due to the diffusion of Li$^+$ on the electrode [48,49]. V$_2$CT$_x$-N sample has the smaller diffusion resistance in low frequency, meaning the better diffusion of Li ion from electrolyte. The straight line in low frequency region of V$_2$CT$_x$-K has a maximum value and slope among four samples. This indicated that the V$_2$CT$_x$-K sample has high impedance, corresponding to the cycling performances of MXene V$_2$CT$_x$ samples electrodes at different current densities.

4. Conclusion

In summary, this paper provides a simple and efficient hydrothermal-assisted etching method to prepare V$_2$CT$_x$ MXene. From analysis of aforementioned results, reaction temperature and time are important factors in influencing the fabrication of V$_2$CT$_x$ MXene. Compared to previous literature [7,34], this method can highly improve the purity and yield of V$_2$CT$_x$ sample. When used as an anode for Li-ion batteries, the as prepared V$_2$CT$_x$ MXene present excellent cycling capability and good reversibility. Among the samples, V$_2$CT$_x$ etching by ammonium fluoride and hydrochloric acid mixed solution can
provide a large electrochemically active surface and a rapid channel for ion and electron transfer with lower resistance, and shows higher specific capacitance with the capacity of 233 mAh g⁻¹ at the current of 1000 mAg⁻¹. Hence, the present study expands on the efficient preparation of V₂CTₓ MXene as an electrode material for high performance Li-ion batteries.

Conflict of interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled, “The preparation of V₂CTₓ by facile hydrothermal-assisted etching processing and its performance in lithium-ion battery”.

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