The Synthesis of High-Quality V\textsubscript{2}C as Electrode Material for Supercapacitors

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ABSTRACT

The two-dimensional V\textsubscript{2}C MXene material has excellent electrical conductivity and a large specific surface area. It has great application potential in the field of energy storage and catalysis. As the electrode material of supercapacitors, V\textsubscript{2}C has the characteristics of electric double layer capacitance similar to carbon materials. In this study, a mixture of sodium fluoride and hydrochloric acid was used as the etching solution, and V\textsubscript{2}AlC was gently etched to get the high-quality V\textsubscript{2}C by a hydrothermal method. The electrochemical results show that the specific capacitance reaches 153.9 F/g in the 1 M Na\textsubscript{2}SO\textsubscript{4} electrolyte at a scan rate of 2 mV/s. This work provides a new method for preparing high-quality V\textsubscript{2}C, promoting the application of V\textsubscript{2}C material in supercapacitors.

Keywords: MXene ; V\textsubscript{2}C; electrode material; supercapacitors

1. INTRODUCTION

Supercapacitors are internationally recognized as a new type of energy storage device between batteries and ordinary capacitors because they have a higher specific power and a longer cycle life than batteries\cite{31}, which have aroused widespread concern for their better energy storage efficiency. According to the different energy storage mechanisms, capacitors can be divided into two types: electric double layer capacitors and pseudocapacitors\cite{31}. The energy storage principle of traditional electric double-layer capacitors is mainly the enrichment of the remaining electric charge on the electrodes. Because the charging or discharging process is mainly a physical process, the long-cycle performance of the electric double-layer capacitor is superior, but the capacity is relatively low. The energy storage of pseudocapacitors is a Faraday process with electrons gain and loss, and the energy density is greatly improved compared with electric double-layer capacitors. Supercapacitors generally have these two mechanisms at the same time, but the ratio of electric double-layer capacitor and Faraday pseudocapacitor in one supercapacitor is different. Pseudocapacitors can be subdivided into three types: fast reversible redox reactions (for example, transition metal oxide/sulfide, such as RuO\textsubscript{2},MnO\textsubscript{2}CoO\textsubscript{2}, NiO and V\textsubscript{2}O\textsubscript{5}\textsuperscript{[3-6]}), Reversible chemical adsorption/desorption such as oxygen adsorption on the surface of gold or platinum; Reversible electrochemical doping/undoping (e.g., polypyrrole, or polyaniline)\textsuperscript{[7]}. At present, the specific surface area of carbon materials with high specific surface area can reach 3000 m\textsuperscript{2}/g, but its actual utilization rate is only about 10 %. The energy storage mechanism of micropores below 2 nm is not clear, which results in the highest capacitance of the final electrode material.

MXene is a new family of two-dimensional layered materials. Since it was first reported by Barsoum and Gogotsi in 2011\textsuperscript{[8]}, MXene has been highly expected in the field of energy storage. MXene is mainly synthesized using a wet method by selectively etching the A phase from the M\textsubscript{n+1}AX\textsubscript{n} compounds. During the etching process, the surface of MXene is usually capped by oxygen (-O), hydroxy (-OH) and fluorine (-F) groups, and thus MXene has been referred to as M\textsubscript{n+1}X\textsubscript{n}TX\textsubscript{x}, where T represents the surface of the end groups (-O, -OH and -F), X is the number of end groups. MXene has high conductivity, surface hydrophilicity and good stability. Many studies have pointed out the application prospects of MXene as electrochemical energy storage materials for lithium ion batteries and supercapacitors. So far, Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x} is the most extensively studied. Besides, V\textsubscript{2}C is another kind of MXene which has been popularly studied recently. However, different with Ti\textsubscript{3}C\textsubscript{2}T\textsubscript{x}, the preparation of high-quality V\textsubscript{2}C is more difficult. Therefore, the facile preparation of V\textsubscript{2}C is still a challenge.

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2. EXPERIMENTAL SECTION

2.1 Chemicals

The chemicals needed in this work are shown in Table 1:

<table>
<thead>
<tr>
<th>Materials</th>
<th>Chemical formula</th>
<th>Molecular mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadium carbide aluminide</td>
<td>V$_2$AlC</td>
<td>140.8</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>36.46</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H$_2$SO$_4$</td>
<td>98.08</td>
</tr>
<tr>
<td>Sodium fluoride</td>
<td>NaF</td>
<td>41.99</td>
</tr>
<tr>
<td>Acetylene black</td>
<td>C</td>
<td>—</td>
</tr>
<tr>
<td>PVDF</td>
<td>(CH$_2$CF$_2$)$_n$</td>
<td>~400,000</td>
</tr>
<tr>
<td>N,N-Methylpyrrolidone</td>
<td>C$_3$H$_9$NO</td>
<td>99.13</td>
</tr>
</tbody>
</table>

2.2 Synthesis of V$_2$C

The V$_2$C was prepared by selective etching Al from the V$_2$AlC (11 Technology Co., Ltd.) powder using the mixture of NaF (Sinopharm Chemical Reagent Co., Ltd.) and HCl (Hangzhou Shuanglin Chemical Reagent Co., Ltd.). Typically, 1 g V$_2$AlC was put into the etching solution which is composed of 50 ml hydrochloric acid and 2 g sodium fluoride, and then it was transferred into a Teflon autoclave after 3-hour pre-reaction in the room temperature. 96 hours later, the high quality V$_2$C was obtained after purification by removing impurities.$^{[9,10]}$

![Fig. 1. The preparation process of V$_2$C](image)

2.3 Synthesis of V$_2$C flexible electrodes

The carbon cloth is used as current collectors for preparing flexible electrodes. Certain amount of PVDF was dissolved in 2 ml NMP, then it was stirred for 12 to 24 hours. Acetylene black and MXene were grinded with a mortar for 10 to 15 minutes to make the mixture uniform powder. The weight ratio of V$_2$C: Acetylene black: PVDF is 8:1:1.$^{[11]}$ The powder mixture was put into the PVDF solution and stirred for another 12 hours to prepare uniform slurry, which was evenly smeared on one piece of carbon cloth (a circle of 8 mm in radius) with a brush for subsequent testing as shown in Figure 2.

![Fig. 2. The V$_2$C/carbon cloth electrode](image)

2.4 Characterization and electrochemical analysis

X-ray diffraction (XRD) patterns of MXene composite were collected using an X-ray diffractometer (Bruker D8 Advance X-ray diffractometer) with Cu-Kα radiation (λ = 1.540 Å). The morphology and elemental mapping of the prepared samples were analyzed with the Scanning Electron Microscope (SEM, a Schottky field emission, JEOL, 4800).

In this work, cyclic voltammetry and impedance testing were performed on the prepared high-quality V$_2$C. The electrochemical measurements were carried out in a three-electrode setup under the potential window of -0.9 ~ -0.1 V in 1 M Na$_2$SO$_4$. Electrochemical techniques such as cyclic voltammetry (CV), galvanostatic charge and discharge (GCD) and electrochemical impedance spectroscopy (EIS) were applied at room temperature (~25°C)$^{[12]}$.

The gravimetric capacitance of the electrodes was calculated using equation (1) by considering the whole area under the CV curves

$$C = \int \frac{I dV}{vm\Delta V}$$                      

Where $I$ is the applied current (A), $\Delta V$ is the potential window (V), $m$ is the mass of the electrode, $v$ is the scan rate (mV/s).
3. RESULTS

3.1 Morphology and structure

In this work, the etching solution composed of sodium fluoride and hydrochloric acid was used to etch $V_2AlC$, and the prepared high-quality $V_2C$ was characterized by XRD and SEM.

The XRD patterns of the original $V_2AlC$, the $V_2C$ before and after removing impurity are shown in Figure 3. It can be observed that the XRD pattern of pure $V_2AlC$ is in good agreement with the standard diffraction peaks of $V_2AlC$ (PDF#29-0101). After etching in NaF/HCl solution, the typical strong peak of $V_2AlC$ at $2\theta=41^\circ$ is almost disappeared. Compared to the V-C bonds, V-Al bonds in $V_2AlC$ are relatively weaker, thus Al atoms in $V_2AlC$ can be easily etched out. Therefore, the peak weakening at $2\theta=41^\circ$ can be a clear evidence of the successful preparation of the $V_2CT_x$. It is also observed that the peak of (002) at around 12.5° shifts to a smaller angle of 7.5°, which indicates that the original matrix was successfully split. However, there are many impurities after solution etching because of the formation of cryolite ($Na_3AlF_14$) compounds during the etching process. High-quality $V_2C$ was obtained after further washing the as-prepared $V_2C$ mixture with dilute sulfuric acid.

The possible reactions during the synthesis and purification processes are shown as below:

\[ 3V_2AlC + 14NaF + 9HCl \rightarrow 3V_2C + Na_3AlF_{14} + 9NaCl + 4.5H_2 \uparrow \quad (1) \]

\[ Na_3AlF_{14} + H_2SO_4 \rightarrow Na_2SO_4 + 3AlF_3 + 3NaF + 2HF \quad (2) \]

It can be seen from the SEM image in Figure 4a that the surface of $V_2AlC$ is rough but unbroken, and its morphology changes significantly after the etching process. As shown in Figure 4b, the morphology of $V_2C$ displays the unique accordion-like structure after the Al layers are etched away from the $V_2AlC$ phase. It is proved that $V_2CT_x$ was successfully prepared by the new etching method. Figure 4c shows the cryolite $Na_3AlF_{14}$ crystals, which are by-products produced during the etching process confirmed by XRD analysis. The pure multi-layer $V_2CT_x$ was obtained by removing the $Na_3AlF_{14}$ crystals with 1 M diluted sulfuric acid at room temperature for 6 hours as shown in Figure 4d.

3.2 Electrochemical performance

Electrochemical tests were carried out by using a three-electrode system in a 1 M $Na_2SO_4$ solution. Figure 5a shows the cyclic voltammetry (CV) of $V_2C$ at different scan rates of 2, 5, 10, 20, 50, 100, 200 mV/s at a potential window of -0.9 ~ -0.1V, and the CV curves present approximately rectangular shape. Obviously, the high-quality $V_2C$ shows the characteristics of an electric double-layer capacitor with a specific capacitance of 153.9 F/g at a scan rate of 2 mV/s.

Figure 5b shows the EIS of the carbon cloth and $V_2C$ electrodes after stability test. $V_2C$ electrode shows series resistance (Rs) of 2.219 Ωm, which is just slightly higher than that of carbon cloth (1.982 Ωm), indicating good electron conductivity and fast ions mobility in the $V_2C$. 

![Fig. 3. XRD analysis of $V_2AlC$ before and after exfoliation.](image)

![Fig. 4. (a) $V_2AlC$, (b) $V_2C$ (c) By-product $Na_3AlF_{14}$, (d) Exfoliated multilayer nanosheets produced by $H_2SO_4$ treatment.](image)
electrodes. Figure 5c shows the GCD plots of V$_2$C material at different current densities. It is observed that those electrodes show very less IR-drop, indicating very good electrode conductivity and less electrode polarization. Figure 5d shows the specific capacity of V$_2$C obtained by GCD test under different current densities. V$_2$C delivers a specific capacitance of 232.5 F/g at a current density of 100 mA/g, which still shows 100.7 F/g at a high current density of 2000 mA/g.

4. CONCLUSIONS
The two-dimensional material V$_2$C, as a new energy storage material, has great application potential in both secondary batteries and supercapacitors. In this work, the high-purity two-dimensional MXene material V$_2$C was successfully prepared by using an etching solution composed of a mixture of sodium fluoride and hydrochloric acid. Electrochemical results show that the high-quality V$_2$C has a large specific capacitance of 153.9 F/g. Therefore, the as-prepared V$_2$C is a good candidate electrode material for supercapacitors.

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REFERENCE