

The Synthesis of High-Quality V_2C as Electrode Material for Supercapacitors

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ABSTRACT

The two-dimensional V_2C 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_2C 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_2AlC was gently etched to get the high-quality V_2C by a hydrothermal method. The electrochemical results show that the specific capacitance reaches 153.9 F/g in the 1 M Na_2SO_4 electrolyte at a scan rate of 2 mV/s. This work provides a new method for preparing high-quality V_2C , promoting the application of V_2C material in supercapacitors.

Keywords: MXene ; V_2C ; 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^[1], 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^[2]. 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_2 , MnO_2 , Co_3O_4 , NiO and V_2O_5 ^[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)^[7]. At present, the specific surface area of carbon materials with high specific surface area can reach 3000 m^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^[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 $M_{n+1}AX_n$ 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 $M_{n+1}X_nT_x$, 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, $Ti_3C_2T_x$ is the most extensively studied. Besides, V_2C is another kind of MXene which has been popularly studied recently. However, different with Ti_3C_2 , the preparation of high-quality V_2C is more difficult. Therefore, the facile preparation of V_2C 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:

Materials	Chemical formula	Molecular mass
Vanadium carbide aluminide	V ₂ AlC	140.8
Hydrochloric acid	HCl	36.46
Sulfuric acid	H ₂ SO ₄	98.08
Sodium fluoride	NaF	41.99
Acetylene black	C	—
PVDF	(CH ₂ CF ₂) _n	~400,000
N,N-Methylpyrrolidone	C ₅ H ₉ NO	99.13

2.2 Synthesis of V₂C

The V₂C was prepared by selective etching Al from the V₂AlC (11 Technology Co., Ltd.) powder using the mixture of NaF (Sinopharm Chemical Reagent Co., Ltd.) and HCl (Hangzhou Shuanglin Chemical Reagent Co.,

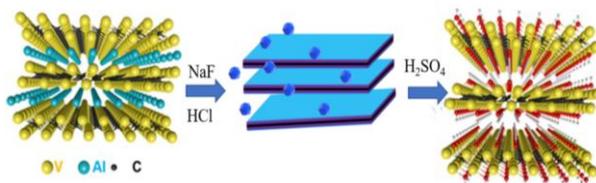


Fig. 1. The preparation process of V₂C

Ltd.). Typically, 1 g V₂AlC 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 V₂C was obtained after purification by removing impurities.^[9,10]

2.3 Synthesis of V₂C 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 V₂C: 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.

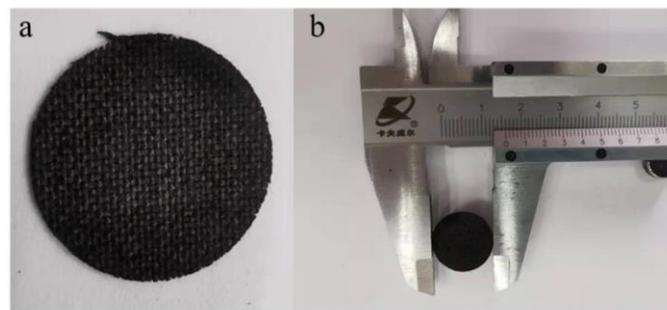


Fig. 2. The V₂C/carbon cloth electrode

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-K α 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 V₂C. The electrochemical measurements were carried out in a three-electrode setup under the potential window of -0.9 ~ -0.1 V in 1 M Na₂SO₄. 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

$$C = \frac{\int IdV}{vm\Delta V} \quad (1)$$

Where I is the applied current (A), ΔV 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

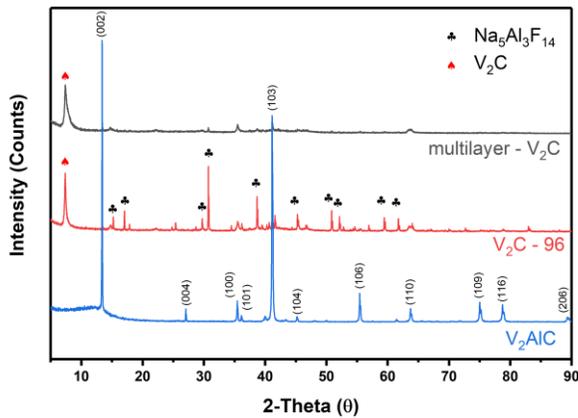


Fig. 3. XRD analysis of V_2AlC before and after exfoliation.

solution, the typical strong peak of V_2AlC at $2\theta \approx 41^\circ$ 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 $2\theta \approx 41^\circ$ can be a clear evidence of the successful preparation 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 ($Na_5Al_3F_{14}$) 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:



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

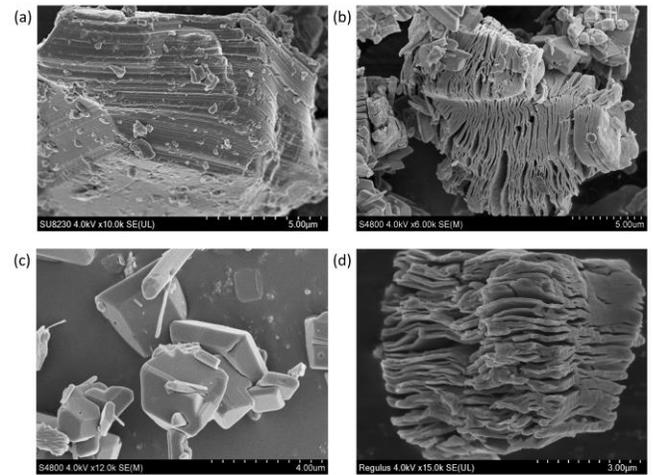


Fig. 4. (a) V_2AlC , (b) V_2C (c) By-product $Na_5Al_3F_{14}$, (d) Exfoliated multilayer nanosheets produced by H_2SO_4 treatment.

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 $Na_5Al_3F_{14}$ 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 $Na_5Al_3F_{14}$ 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 $-0.9 \sim -0.1V$, 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 (R_s) of 2.219 ohm, which is just slightly higher than that of carbon cloth (1.982 ohm), indicating good electron conductivity and fast ions mobility in the V_2C

electrodes. Figure 5c shows the GCD plots of V_2C material at different current densities. It is observed that those

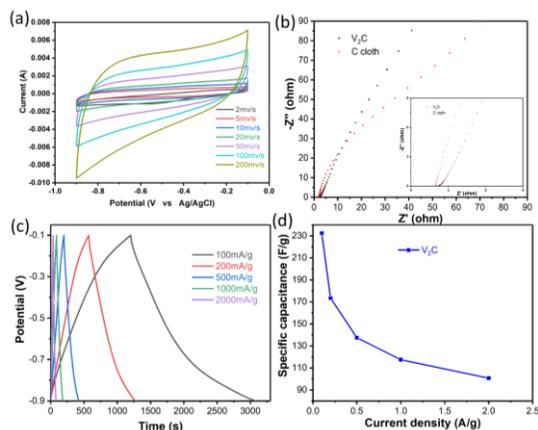


Fig. 5. (a) CV diagram of V_2C , (b) Nyquist plots of V_2C and carbon cloth, (c) GCD curves of V_2C , (d) specific capacity of V_2C under different current densities.

electrodes show very less IR-drop, indicating very good electrode conductivity and less electrode polarization. Figure 5d shows the specific capacity of V_2C obtained by GCD test under different current densities. V_2C 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_2C , 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_2C 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_2C has a large specific capacitance of 153.9 F/g. Therefore, the as-prepared V_2C is a good candidate electrode material for supercapacitors.

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