Application of New Mxene Based Materials in Electrochemical Sensors

Xiang Zhang *, Yu Gu

Nantong Ecological Environment Monitoring Center, Nantong, Jiangsu, 226000, P.R. China

*Corresponding author. E-mail: hbj@nantong.gov.cn

These authors contributed equally to this work.

Abstract. In the current research on the application of new Mxene based materials in electrochemical sensors, the research on the charge storage of new Mxene based materials is not comprehensive enough. The charge storage of new Mxene based materials under different scanning rates is studied in the form of experiments. According to the needs of the experiment, experimental reagents and instruments were selected to prepare Mxene solution and new Mxene based materials. Macroporous Mxene was prepared as the electrode of EES device to store and convert energy. The enzyme was immobilized on the inner surface of Ti3C2Tx to sense biological activity. The experimental results show that the charge storage performance of the new Mxene based materials is the best when the scanning rate is 15mVs-1, which is the most suitable for electrochemical sensors.

1. Introduction

Electrochemical sensors are used to analyze and measure target molecules or substances qualitatively or quantitatively by measuring their electrical and electrochemical properties. Electrochemical sensors originated in the 1950s, with the development of science and technology such as electrochemistry, microelectronics and material processing. In the 1960s, with the advent of ion selective electrode and enzyme electrode, electrochemical sensor entered a stable development stage.[1-3]. Electrochemical sensor consists of two parts: sensor and converter. The sensor has two main functions: selectively interact with the object to be measured, and then convert the measured chemical parameters into conduction module, which can generate response signals. Finally, the response signal of the identification platform is transformed into the signal that can be used for analysis, and the quantity of the object to be measured in the new Mxene based material is detected [4-6]. With the continuous consumption of fossil fuel resources and the increasingly prominent environmental problems, people begin to turn their attention to sustainable and renewable clean energy. Since the beginning of the 21st century, with the in-depth understanding and development of the unique properties of new Mxene based materials, Nano science and technology have developed rapidly in energy, biology, aerospace and other fields [7,9]. Graphene as a representative of two-dimensional materials has some properties that three-dimensional bulk materials do not have, such as the reduction of the size of the surface area is greatly increased than the bulk materials, more atoms are exposed to the surface, thus showing higher electrochemical reaction activity, so two-dimensional nano materials quickly become a research hotspot in the field of energy storage. At present, the literature on the application of new Mxene based materials in electrochemical sensors is not very rich, which needs further study.
2. Experimental preparation

2.1. Selection of experimental reagents and instruments

According to the needs of the experiment, the experimental reagents and instruments are selected as shown in Table 1:

| Laboratory instruments / reagents | Laboratory instruments / reagents | manufacturer | manufacturer |
|----------------------------------|----------------------------------|--------------|--------------|
| CHI-660D electrochemical workstation | glucose | Shanghai Chenhua Instrument Co., Ltd | Sinopharm group |
| KQ218 ultrasonic cleaning instrument | Magnesium chloride | Kunshan Ultrasonic Instrument Co., Ltd | Sinopharm group |
| Vacuum drying oven | potassium chloride | Shanghai Yiheng Scientific Instrument Co., Ltd | Sinopharm group |
| Tubular resistance furnace | hydrofluoric acid | Shanghai Yafeng Furnace Co., Ltd | Shanghai McLean Biochemical Technology Co., Ltd |
| DC high voltage generator | Restore sweet skin | Beijing Institute of mechanical and electrical high voltage Technology Co., Ltd | Sinopharm group |
| Microinjection pump | Anhydrous ethanol | Baoding Lange constant flow pump Co., Ltd | Sinopharm group |
| Electronic balance | Tetramethylbenzidine | Shanghai Precision Instrument Factory | Shanghai Yuanye Biotechnology Co., Ltd |
| DLMAX-2200 X-ray diffractometer | Fluorination theory | Japan Science Corporation | Shanghai prosace group |
| Disodium hydrogen phosphate dodecahydrate | hydrochloric acid | Sinopharm group | Sinopharm group |
| Disodium phosphate dihydrate | L-cysteine | Sinopharm group | Sinopharm group |

Based on the above experimental instruments and reagents, mxene solution and new mxene based materials were prepared.

2.2. Preparation of Mxene solution

Adding 15 ml 12 m HC and 0.99 g LIF into 70 ml polypropylene plastic bottle, and stirring for 5 min to dissolve LIF in HCl. In order to prevent the system from overheating, 1 g Ti₃AlC₂ was added to the above solution several times. Then, the plastic bottle was transferred to a collector type magnetic stirrer and stirred at 35 ℃ for 24 h to complete the etching of A1 layer atoms. After the reaction, the product was transferred to an 80 ml centrifuge tube, centrifuged at 6200 rpm and washed with water until the pH of the supernatant was close to neutral. The precipitate centrifuged to neutral was redispersed in water, and then ultrasoniced at 220W for 40 min in hydrogen atmosphere. After centrifugation at 6200rpm for 1h, the supernatant was collected to obtain ti3c2tx solution, which was put into hydrogen for storage.

2.3. Preparation of new Mxene based materials

Diluting the solution containing 100 mg Mxene material to 300ml, add 0.24g, and then ultrasonic wave for 10 minutes to dissolve it. Weigh 0.1g dopamine hydrochloride in the mixed solution and stir it for 24 h at room temperature to complete the self polymerization of dopamine hydrochloride. After
centrifugation at 8000 rpm for 5 min, the precipitates were collected and freeze-dried for 48 h to obtain three-dimensional polydopamine coated Mxene materials. Then, the orange Mxene was coated with polydopamine. The three-dimensional carbon coated Mxene material, named T-Mxene@C, was prepared by carbonizing the polydopamine layer after being treated at 700 °C for 2 h in hydrogen atmosphere Mxene. The specific preparation process. In addition, the Mxene powder obtained by direct freeze-drying of Mxene solution was taken as the reference sample, which was recorded as f-Mxene. The powder of f-Mxene after high temperature treatment at 700 °C was also taken as the reference sample, which was recorded as h-Mxene.

3. Experimental process

3.1. Storing and converting energy

Mxene modules were initially mainly used in the field of supercapacitors, and then extended to other alkali metal ion energy storage fields. Therefore, it is necessary to develop more advanced structures for high performance electrodes based on Mxene. Gogotsi group used PMMA as template to prepare macroporous Mxene as electrode of EES device. Because the ion transport path is significantly shortened, it has ultra-high rate capability. Similarly, the vertical alignment of Mxene nanosheets can also be much shorter than that of 2D structure ion transport path, and show a thickness independent rate capability, up to 200 μM. Recently, many researches have focused on assembling 2D mxene nanosheets into 3D macrostructures. With the customized 3D network and 3D components, it provides fast ion transport path and high utilization of active sites, so it has excellent electrochemical performance. Therefore, a more comprehensive study of novel 3D assembled Mxene structures is needed to better understand and explore its energy storage applications. Compared with Mxene film, 2D Mxene hybrid film and reduced graphene oxide film electrode, the above Mxene electrode showed a significant increase in capacitance and transmission rate. The formation of 3D interconnection network during gelation can effectively limit the re stacking of MXene nanosheets, thus providing an interconnection network for fast ion transport and providing high electrical conductivity.

3.2. Shielding and absorbing electromagnetic waves

Due to its unique structure and properties, many Mxene materials and Mxene composites have excellent electromagnetic wave attenuation properties. The self-supporting materials etched by HCl + LIF exhibit high conductivity due to low inter chip resistance and in-situ Li ion doping. Further research shows that the shielding effect of electromagnetic wave can reach 92 dB. In addition, the doping of other components in Mxene materials is becoming more and more popular. Similar Fe doped Ti3C2Tx Mxene films show an effective reflection loss of -57.3 dB at 10.1 GHz at a thickness of 1.9 mm, and a broadband reflectivity of less than -10 dB in the range of 9.1 GHz to 11.1 GHz. In addition, Mxene @ polystyrene microspheres with high conductivity (1081 s / M) were prepared by electrostatic assembly, and they have electromagnetic wave shielding performance of more than 54 dB in the whole X-band. With the load increasing to 1.90% Vo1, the electromagnetic wave absorption can be further improved to -62 dB. 3D porous Mxene based aerogels with high reflectivity and high conductivity are very suitable for shielding and absorbing electromagnetic waves. The 3D macrostructure generated by the cross-linking of nanosheets also has porous structure, so it is expected to increase the electromagnetic wave loss ability of nanosheets. The hole wall composed of Mxene nanosheets with good dielectric and magnetic properties can increase the energy loss in the electromagnetic wave, so as to achieve the effective attenuation of the electromagnetic wave. All in all, Mxene materials have great potential in the field of electromagnetic wave shielding and absorption.

4. Experimental result

In order to test the electrochemical performance of the new MXene based materials, according to the mass ratio of 8:1:1, appropriate amount of active material (Ti3C2 MXene, 2H-MoSz), binder and conductive agent were respectively weighed and put into the agate mortar, and then appropriate amount
of NMP was dripped, and then fully ground to obtain uniform slurry. Finally, the slurry was evenly coated on the carbon paper. The coating area is about 1 cm × 5 mg. The electrodes were then dried in a vacuum oven at 45 ℃ for 12 hours. The Ag / AgCl electrode was selected as counter electrode and reference electrode respectively. The voltage window of cyclic voltammetry test (CV) is -1.0v-0v, and the voltage window of constant current charge discharge test is -1.0v-0v. Electrochemical impedance analysis was performed in the frequency range of 100 kHz ~ 0.01 Hz. The specific capacity of the electrode can be calculated according to the GCD curve, the formula is as follows:

\[ W = \frac{h \Delta j}{Q} \]  

(1)

In formula (1), \( h \) is the mass specific capacitance, \( j \) is the potential window, and \( Q \) is the scanning rate. On the basis of formula (1), according to the CV Curve, the calculation formula of specific capacitance is obtained as follows:

\[ R = \frac{1}{\Delta k} \int \frac{h}{t} \]  

(2)

In formula (2), \( h \) is the mass specific capacitance, \( k \) is the potential, and \( t \) is the point current density. In addition, the coulomb efficiency curve is expressed by GCD curve, the specific expression formula is as follows:

\[ \delta = \frac{E}{P} = \frac{r_1}{r_2} \]  

(3)

In formula (3), \( E \) represents discharge capacity, \( P \) represents charging capacity, \( r_1 \) represents discharge time and \( r_2 \) represents charging time. According to the formula (3), the preparation of PVA-H₂SO₄ gel was carried out. When PVA- H₂SO₄ gel is solidified at room temperature, 12h, a symmetrical flexible all solid state supercapacitor based on a new MXene based material can be obtained. The specific capacitance of the device based on the active material area can be calculated by the charge discharge curve:

\[ D = \frac{U \times \Delta g}{H \times \Delta y} \]  

(4)

In formula (4), \( U \) is the constant discharge current, \( H \) is the opposite area of the active material on the two working electrodes, \( g \) is the discharge time, and \( y \) is the constant discharge current. The energy density of Mxene based flexible all solid state supercapacitors is calculated

\[ F = \frac{1}{(2 \times 3.6)} \times \eta \times C^2 \]  

(5)

In formula (5), \( \eta \) represents the voltage window of the charge discharge curve, and \( C \) represents the discharge time of the device. Cycle stability is one of the important parameters to evaluate the performance of supercapacitors. In order to study the stability of the material in electrochemical test, the cyclic stability of the electrode was tested at high current density of 50ag⁻¹. After 10000 cycles, the specific capacitance of the electrode decreases slightly, which is 96.8%, which may be due to the gradual activation of the electrode surface in the electrolyte. A large number of practical results show that the new Mxene based materials have the best application effect in electrochemical sensors when the charge storage is between 81% and 85%. On the basis of the above, the charge storage of the new Mxene based materials at three different scanning rates under the same electrode conditions was tested, and the experimental results are shown in Fig. 1-3
As shown in Figure 1, when the scanning rate is 5mVs\(^{-1}\), the charge storage capacity is 76.5%; As can be seen from Figure 2, when the scanning rate is 15mVs\(^{-1}\), the charge storage is 84.5%; According to figure 3, when the scanning rate is 25mVs\(^{-1}\), the charge storage capacity is 89.5%, which indicates that the charge storage capacity performance of the new Mxene based material is the best when the scanning rate is 15mVs\(^{-1}\).

5. Conclusions
Through the preparation of Mxene based electrode materials for supercapacitors, the electrochemical performance and energy storage mechanism of these materials were studied. Combined with our understanding of the current research situation of these materials and the existing work basis, we can
carry out the next work in the following aspects.1 NiCoAl-LDH and 1T MoS2 were peeled to prepare a few or even single layer of nanosheets, and then the nanosheets were compounded with new Mxene based materials to prepare heterostructures. This Mxene based heterostructure will have more interfaces, which is beneficial to the improvement of electrochemical performance. 2 It can also peel the Mxene micro sheet to obtain a few layers of Mxene sheet, and composite with the stripped NiCoAl-LDH and 1T MoS2 nano sheet to explore the performance of the material for supercapacitor. 3 Both transition metal nitrides and transition metal carbides have ultra-high conductivity, and the former also has high theoretical specific capacity, which belongs to the electrode materials (high power density and energy density) in supercapacitors. It enriches the academic literature on new Mxene based materials, and provides new ideas for the application research of related types of materials. Due to the limited research conditions, there are still some deficiencies in this study, which will be improved in the future.

Acknowledgment
This work was supported by Nantong Social Livelihood Science and Technology Project: Preparation and electrochemical response of functional mxene based conductive composites for rapid detection of contaminants in food.

References
[1] Sasal A, Tyszczuk-Rotko K, M Wójciak, et al. (2020) First Electrochemical Sensor (Screen-Printed Carbon Electrode Modified with Carboxyl Functionalized Multiwalled Carbon Nanotubes) for Ultratrace Determination of Diclofenac[J]. Materials, 13(3):781.
[2] Yang L, Wang J, H Liu, et al. (2021) Electrochemical sensor based on Prussian blue/multi-walled carbon nanotubes functionalized polypyrrole nanowire arrays for hydrogen peroxide and microRNA detection[J]. Microchimica Acta,188(1):1-12.
[3] Bojdi M K, Behbahani M, Ranjbari S. (2020) Developing an Electrochemical Sensor Based on Modified Siliceous Mesocellular Foam for Efficient and Easy Monitoring of Cadmium Ions[J]. ChemistrySelect, 5(22):6617-6625.
[4] Zhou T, WANG L, NIU Q. F. (2020) Research on Electromagnetic Field Simulation and Electrode Position Detection Method of Submerged Arc Furnace[J]. Computer Simulation, 37(5): 206-212.
[5] Pi M, Jiang L, Wang Z, et al. (2021) Robust and ultrasensitive hydrogel sensors enhanced by MXene/cellulose nanocrystals[J]. Journal of Materials Science, 56(14):8871-8886.
[6] Chen Y, Wang Y, Luo Y, et al. (2019) Realization of Artificial Neuron Using MXene Bi-Directional Threshold Switching Memristors[J]. IEEE Electron Device Letters, PP(99):1-1.
[7] Eom W, Shin H, Ambade R B, et al. (2020) Large-scale wet-spinning of highly electroconductive MXene fibers[J]. Nature Communications, 2020, 11(1):2825.
[8] Cui G, Sun X, Zhang G, et al. (2019) Electromagnetic absorption performance of two-dimensional MXene Ti_3C_2T_x exfoliated by HCl + LiF etchant with diverse etching times[J]. Materials Letters, 252(OCT.1):8-10.
[9] Ayman I, Rasheed A, Ajmal S, et al. (2020) CoFe2O4 Nanoparticle-Decorated 2D MXene: A Novel Hybrid Material for Supercapacitor Applications[J]. Energy And Fuels, 34(6):7622-7630.
[10] Liu P, Chen S, Yao M, et al. (2020) Double-layer absorbers based on hierarchical MXene composites for microwave absorption through optimal combination[J]. Journal of Materials Research, 35(11):1-11.