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A Review of the Application of Two-dimensional MXene Materials

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Abstract

In every stage of human development, energy always plays a vital role, from bronze, gold, to modern oil and gas mining, and then to modern electric energy, wind energy research, every step of energy development, often promote the progress of human society. In the past time, people relied on the burning of fossil fuels, gradually entered the industrial age, changed the production mode from human operation to machine operation, and entered the high-speed information age from the preparation and application of semiconductors and optical fibers. However, with the development of The Times, the structure of energy, application and human demand for energy have changed, relying solely on the burning of fossil energy gradually can not meet all the application needs. Moreover, for the excessive consumption of non-renewable energy, the discharged sewage and waste will seriously affect the ecological environment and the world economy, and the low application rate and low purity products produced will also increase the production cost and reduce the production profit. Therefore, it is necessary to develop a new energy material, which can provide excellent performance at the same time, but also play a role in protecting the ecological environment. New energy materials refer to a class of materials that are being developed and can meet a variety of energy sources and technologies. For example, previously developed solar cell materials, hydrogen storage materials, nanomaterials, fuel cell materials and so on. However, the nanoparticles in nanomaterials can be assembled into systems with mesoporous solids. Due to the characteristics of the nanoparticles themselves and some new effects of coupling with the matrix at the interface, they have become the focus of recent research.

Keywords

New Energy Materials; Nanomaterials; Interface Coupling.

1. Introduction

Since the 21st century, with the progress of science and technology and industry, environmental pollution and energy crisis have become major problems to be solved urgently. The uncontrolled exploitation and inefficient abuse of traditional fossil fuels (coal, oil and natural gas, etc.) are endless, and the pollution of the environment and the waste of resources are bound to attract people's attention. The new energy developed with the development of science and technology can not only well solve the problems of fossil fuel depletion, energy crisis and global warming, but also provide the basic guarantee for the comprehensive implementation of "low-carbon policy" and the realization of "low-carbon economy". However, the application of new energy is also accompanied by inevitable defects - intermittency, volatility and randomness, which limits the stability of its energy output, resulting in inefficient use and waste of energy [1]. Therefore, it is necessary to develop new electrochemical energy storage devices that can efficiently store and convert these unstable energy sources. The energy is converted to form a separate self-powered unit, in which the storage method of energy is worth paying attention to.

At present, in the research direction, the most concerned micro electrochemical energy storage devices are lithium-ion micro batteries or thin film batteries. This type of battery has a high energy density and can meet the needs of portable, mobile and flexible wearable devices [2, 3]. But in power density [4], long cycle life [5] and safety and other aspects are slightly lacking [6], it is difficult to meet the needs of long-term and high power work [2-7]. Therefore, the research and development of supercapacitors came into being.

Supercapacitor is a new type of high power electrochemical energy storage device. It is a new way of storing charge and circulating power supply by pseudo capacitor or double layer capacitor, which has entered the modern research field. Its own high power density and long cycle life make it gradually become a better candidate for microelectronics energy storage components. Compared with battery-class materials, although there is a gap in energy density, the higher power density and long cycle life make it more suitable as an energy storage device for microelectronics, such as the use of supercapacitors for regenerative braking in some cars, which charge and discharge faster than battery-class materials, and have a higher power density. In addition, their energy storage capacity is much greater than that of conventional capacitors. As a result, they are better suited to store kinetic energy when the vehicle slows down and release it when it suddenly accelerates. Because electrons can travel back and forth quickly, they are high-power devices even though they can't store a lot of energy[8-10]. Supercapacitors are mainly composed of electrode materials, electrolytes and diaphragms. Among them, the electrode material is the most influential factor to the supercapacitor, and the key to determine the performance of the electrode material is the structure of the material[11].

Electrode materials usually include transition metal compounds, carbon materials, conductive polymers and their mixtures. In addition to the above electrode materials, the 2D transition metal carbides, nitrides and carbon nitrides family MXene also show great potential in the application of supercapacitor electrode materials [12, 13]. Derivative material refers to a simple compound in which the atoms or atomic groups contained in themselves are replaced by other atoms or atomic groups to produce more complex products. Taking methane (CH4) as an example, methanol (CH3OH) and acetic acid (CH3COOH) are all derivatives of methane. Compared with the precursor material, the generated derivative material not only introduces foreign atoms or atomic groups, but also introduces defects in the preparation process and changes the structure of the material. Thus, the prepared derivative materials have more reaction sites and stronger reactivity.

2. 2D Materials MXene Overview

MXene is a novel two-dimensional lamellar material, first developed by Gogotsi [14, 15] It was synthesized and first reported in 2011, and has gradually come into the eyes of researchers due to its unique accordion structure and novel characteristics. Due to its many outstanding properties, such as mechanical properties, metal conductivity, and unique in-plane anisotropic structure, MXene is fast becoming the forefront of two-dimensional materials research and has been applied in many fields. Especially in the field of electrochemical energy storage, two-dimensional MXene materials can be used as electrodes, additives, partitions, or carriers. So far, about 30 different types of MXene with good structure and unique properties have been successfully prepared, and with the development of more theoretical research, the application field of MXene is gradually enriched.

2.1 Structure of MXene Material

MXene is usually prepared by selective etching of its precursor, A ternary carbon-based or nitrogenous compound called $M_{n+1}AX_n$ phase, using a hydrofluoric acid solution to remove its A-element (usually Al or Ga) [16] (As shown in Figure 1). The chemical formula of MXene obtained after etching is summarized as $M_{n+1}AX_n$, where M refers to the transition metal (e.g. Sc, Ti, V, Cr, Zr, Hf, Nb, Mo, Ta, and W), X is carbon or nitrogen, and T represents the surface functional group (e.g. -O, -OH, -F, -Cl). The reaction equation is as follows (take $Ti_3C_2T_x$ as an example)[14]:

$$\mathrm{Ti_3AlC_2 + 3HF = AlF_3 + 3/2\,H_2 + Ti_3C_2} \tag{1}$$

$$\mathrm{Ti_3C_2 + 2H_2O = Ti_3C_2(OH)_2 + H_2} \tag{2}$$

$$\mathrm{Ti_3C_2 + 2HF = Ti_3C_2F_2 + H_2} \tag{3}$$

It can be seen that the MAX phase generates Ti_3C_2 after HF etching, and part of Ti_3C_2 will continue to react with HF and H2O to generate part of $Ti_3C_2T_x$ and $Ti_3C_2(OH)_2$.

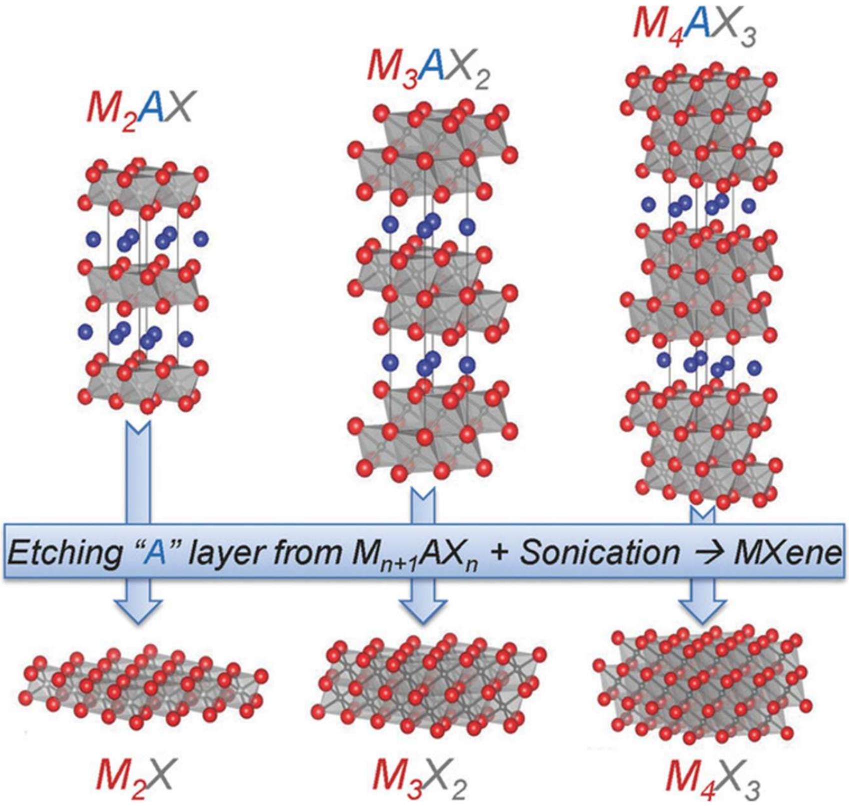

Figure 1. Flow chart of MXene synthesized by MAX phase etching [16]

2.2 Application of MXene

MXene has a different accordion morphology from other two-dimensional materials [16, 17] As shown in Figure 2, the unique P-layer structure facilitates its electronic transmission and is also due to its high electrical conductivity (2.4×10^4 S/cm).[18, 19] The properties are often used in supercapacitors [20-23]. Such as the Husam N. Alshareef team [20] The prepared MXene-on-Paper electrode material can still maintain 92% capacity retention rate and close to 100% coulomb efficiency after 10000 cycles of charge and discharge at the current density of 2mA/cm^2. (Figure 3) The prepared capacitor device has a power density of 46.6 mW/cm^2 and an energy density of 0.77μWh/cm^2, which is relatively high compared to other MXene capacitor materials. he ANPY/MXene electrode material developed by Zhang's team[22] has a high specific capacitance of 451.75F/g. In the flexible test of different angles after assembly into devices, the shape of CV curve remains consistent, indicating that it has good flexibility. The capacity retention rate of 91.8% also shows good cycle stability and capacitive performance, with a maximum power density of 9.72W/kg and an energy density of 399.99Wh/kg, which is the leading level compared to other MXene capacitors (Figure 4).

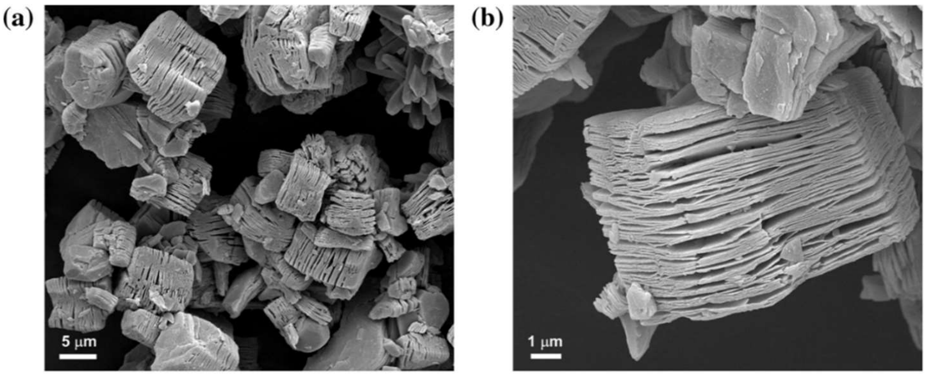

Figure 2. SEM scan of MXene accordion structure [17]

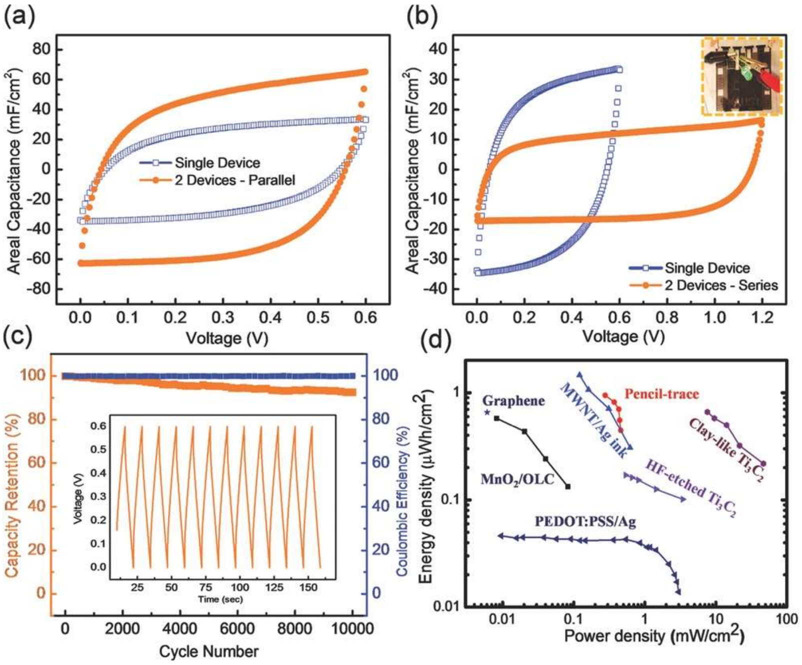

Figure 3. Performance test diagram of MXene-on-paper capacitor [20]

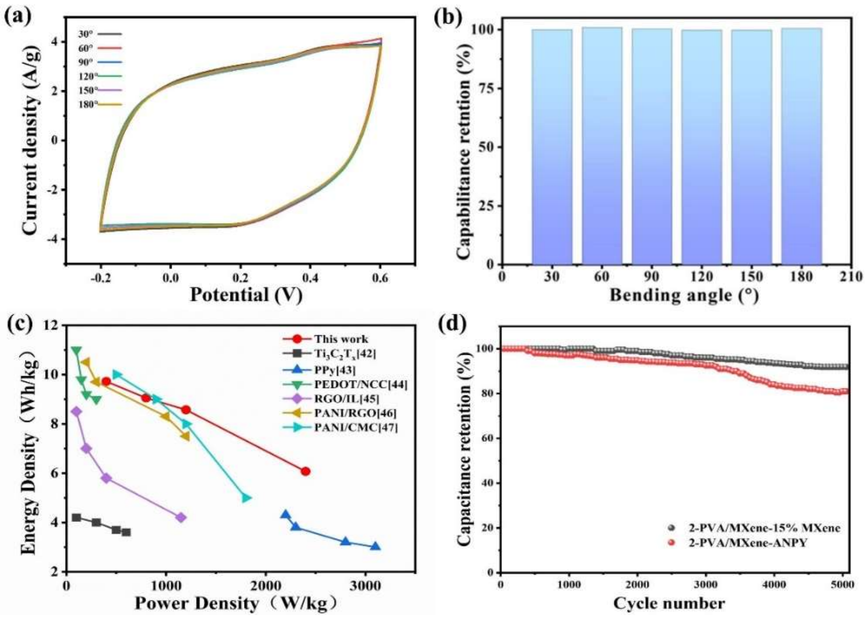

Figure 4. Performance test diagram of ANPY/MXene capacitors [23]

Monolayer MXene is also characterized by its high specific surface area (1000 m^2/g) as well [24, 25] high mechanical properties (386 GPa)[26-28] often used in sensors [29-32], electromagnetic shielding [33-35] other aspects, For example, Zhou's team[36] constructed a TiO_2/MXene/Cds heteronode sensor to detect carcinoembryonic antigen (CEA) in human serum, as shown in Figure 5(a). In the linear regression curve of the sensor, the correlation coefficient was 0.998, and the CEA concentration was calculated to be 0.24fg/mL. It demonstrated good sensitivity and selectivity for CEA in the presence of other interfering substances (Figure 5(b)), and signal stability under prolonged repetitive illumination reflects the good stability of the proposed biosensor. The basically stable corresponding current of the sensors prepared in different batches also indicates that the sensor has good cycle stability and obvious repeatability.

Due to the high conductivity of MXene, it can effectively conduct the energy of electromagnetic waves, less its transmission, and the unique layered structure also contributes to the repeated reflection and absorption of electromagnetic waves, thereby improving the efficiency of electromagnetic shielding. MXene itself can be used as the preferred material for electromagnetic shielding. With the development of research and development, MXene is gradually compatible with other materials. For example, some polymers, carbon derivatives, nano-ferrites and metal mailing frames are used as composite materials and electromagnetic shielding. For example, Kim et al [37] MXene/ Plasticized polyurethane (MX/APU) composite foams for electromagnetic shielding and impact absorption were prepared using a vacuum filtration method with an electromagnetic shielding efficiency of 76.2 dB, making them the best choice for lightweight applications. Qu et al[38]. used silver nanosheets (as reflectors), MXene(as loss layer) and silver nanowires (as heat conduction and shielding layer) to successfully prepare a multi-heterolayer high-performance flexible electromagnetic shielding functional composite material. The coating weight was only $25g/m^2$, and the EMI shielding value of the composite material reached 70.96dB. Chang et al [39] on this basis, MXene/AgNWs/PEDOT composite coating was prepared by drip casting method. 76.6wt% MXene/AgNWs/PEDOT: The PSS coating showed the best performance, and the electromagnetic interference shielding performance of the coating showed high stability against bending cycles after 800 bending cycles.

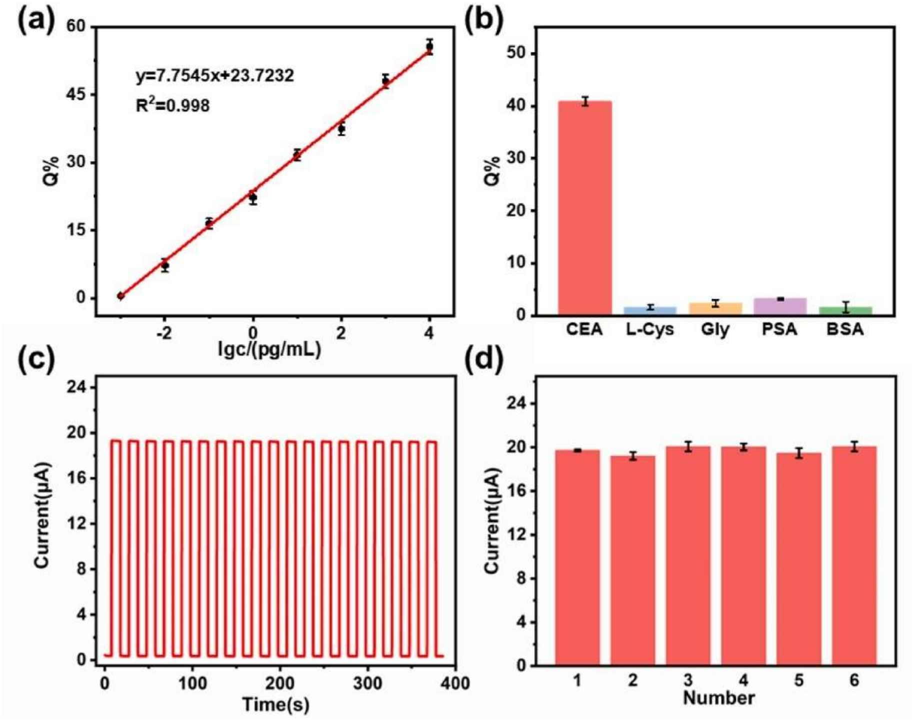

Figure 5. Performance test diagram of TiO_2/MXene/Cds heterojunction sensor [36]

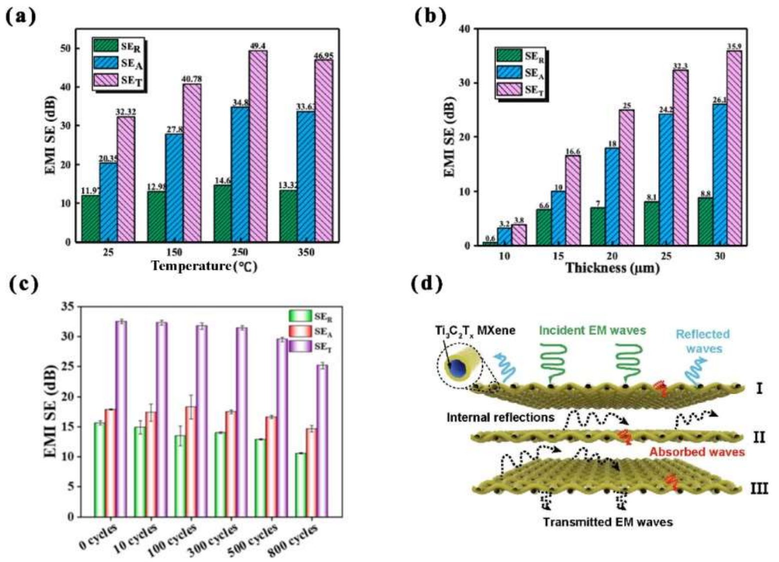

Figure 6. Performance test diagram of electromagnetic shielding of MXene/AgNWs coating [38, 39]

3. Overview of Derivatives

"Derivative" usually refers to the substitution of atoms or atomic groups contained in a certain raw material or compound by chemical reaction or physical modification to generate other atoms or atomic groups, thus generating more complex new materials. For example, the strength and toughness of the material can be significantly improved by alloying or composite materials [40-42], by doping or modification, the electrical or thermal conductivity of the material can be improved [43-45], the prepared derivatives of this kind can have different properties and more efficient functions, so they have been widely used in various fields.

3.1 Application of Derivative Materials

Because of their more efficient properties than raw materials, derivatives are widely used in many fields. For example, in the medical field, new compounds such as chitosan and its derivatives are often obtained by chemical modification of polysaccharide molecules [46] chitosan has been extensively studied due to its unique antibacterial, antitumor and immunomodulatory properties. In addition, chitosan can also be used as a drug delivery carrier in the form of hydrogels, sponges, microspheres, nanoparticles and films to treat diseases, especially skin and soft tissue diseases, such as skin, muscle, blood vessel and nerve injuries and lesions. The insoluble and unstable properties of chitosan in water limit its further development, and a team prepared its derivatives by means of chemical modification [47, 48], while retaining the effective biological properties of chitosan, the physical and chemical properties of chitosan are improved, and different medical materials are prepared and widely used in the treatment of different diseases.

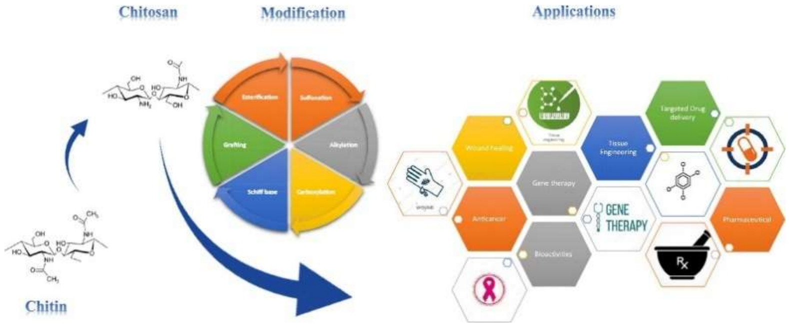

Figure 7. Application of chitosan derivatives [49]

In addition to the medical field, derivative materials also have significant application prospects in electrochemical energy storage and energy conversion. For example, MOF-based organic frameworks can be flexibly regulated according to their basic molecular components, and superstructures with hierarchical porosity, hierarchical structure and hierarchical combination can be constructed. These structural properties make MOF derivatives have abundant active sites, huge specific surface area and a variety of ion dispersion channels, which is conducive to improving electrical conductivity and rapid electron transfer [50-52], Xu's team, for example [53] Fe/Ce doped MOF derivatives were prepared by calcination, which catalyzed ozone and degraded hexazinone efficiently. Compared with other catalytic materials, the removal rate of hexazinone was 78.78% within 20 minutes. The first-order kinetic constants (KOBS) are 6.71, 12.70 and 12.00 times higher than O_3, respectively, and the degree of TOC mineralization is 42.37%. After the test, the content of metal ions in the solution is low, indicating that the derivative materials prepared by KOBS have strong catalysis, ore forming ability, good stability and green safety. The electrochemical test also shows that it has strong charge transfer ability and catalytic performance.

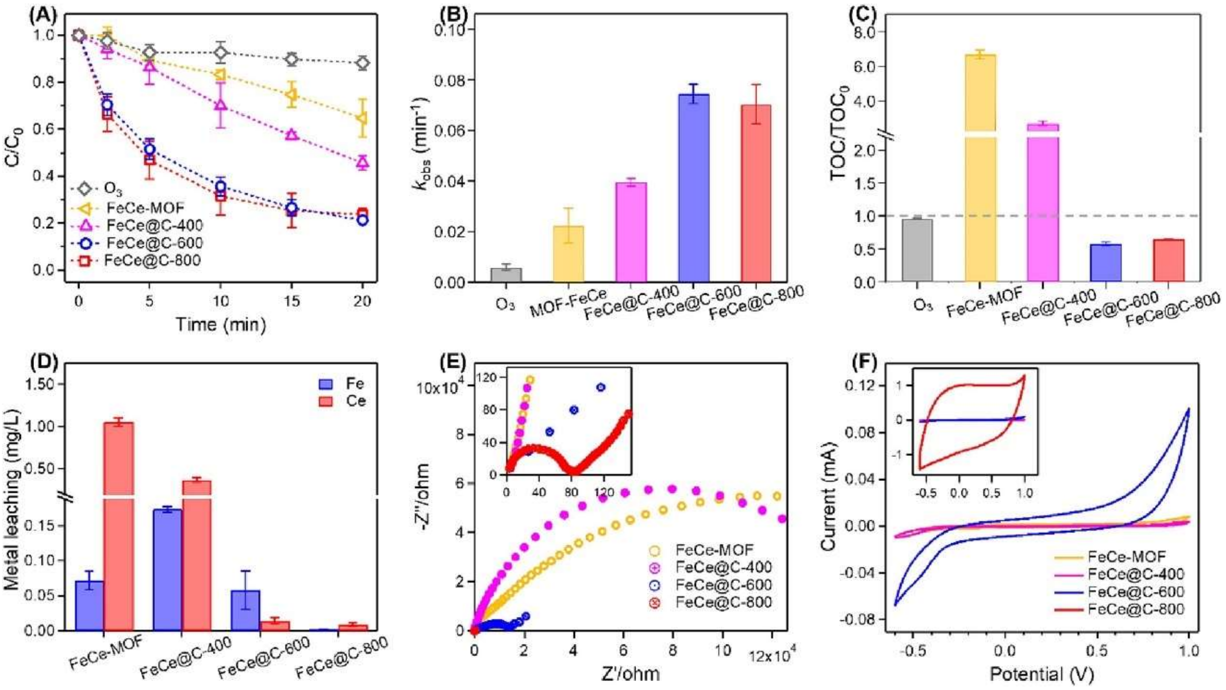

Figure 8. Performance test of Fe/Ce-MOF derivative materials [53]

Li et al. [54] ZIF-67 was used as the precursor and was continuously carbonized and etched under an inert atmosphere to obtain N-doped porous carbon materials. By controlling the annealing temperature, the doping content of pyridine N was further controlled to obtain a derivative material with high pyridine N-doped MOF with abundant defects. The performance test was shown in Figure 9. The contours of CV curves at different sweep speeds consistently reveal that the material has a good charge response ability. It can be seen from the reaction kinetics curves that the potassium storage behavior of these NPCS is dominated by surface-driven processes. NPC-600 shows the highest b value and the highest pseudo capacitance contribution, with surface-led processes accounting for 78.3%. The authors prepared MOF derivative materials by doping. The addition of N and the formation of defects enhanced the conductivity of the material itself, and created additional active sites for the transmission and storage of K^+, which improved the reactivity and enhanced the electrochemical capacity.

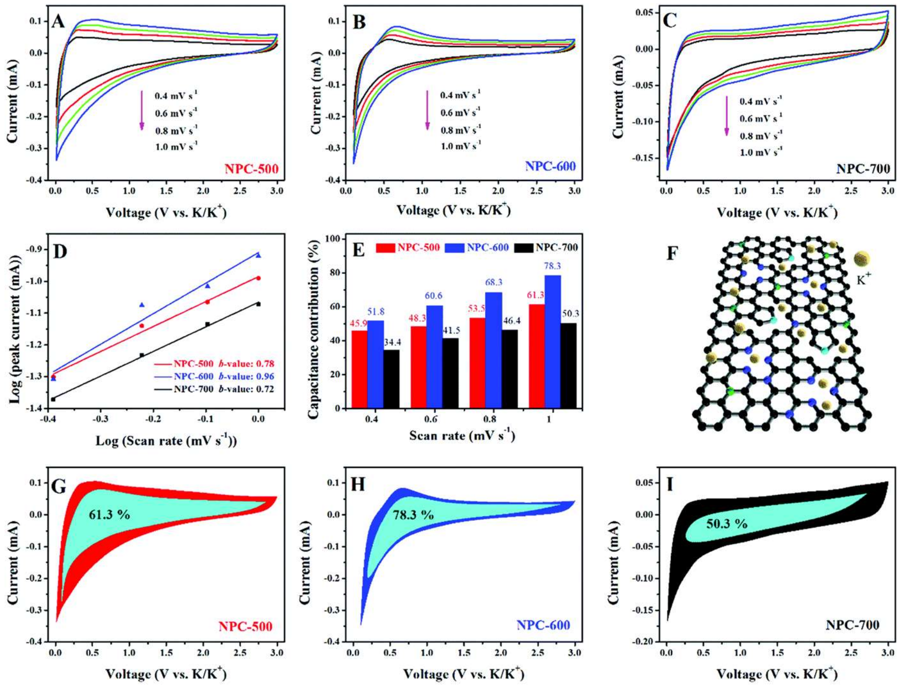

Figure 9. Electrochemical performance test diagram of N-doped samples [54]

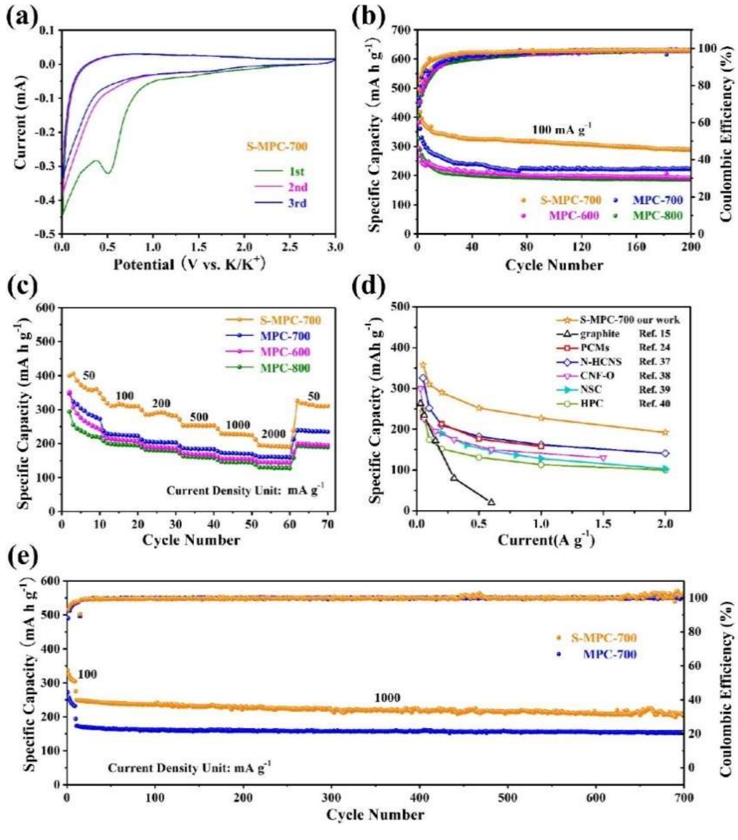

Figure 10. Electrochemical performance test diagram of S-doped samples [55]

Zuo et al ,[55] a method of secondary heat treatment of Fe-MOF to achieve S-doping is reported, so as to form S-doped flower-shaped porous carbon materials. The prepared S-MPC-700 anode material has an excellent reversible capacity of up to 298mAh/g, which further proves that doping of S provides abundant active sites for K^+ storage, expands the layer spacing, and promotes the embedding/removal of K^+. The good magnification and cycling properties prove that the material has good electrochemical properties.

3.2 Application of MXene Derivatives

As a new two-dimensional nanomaterial, MXene is used in supercapacitors due to its high electrical conductivity and charge transfer ability brought by its unique accordion structure [56-58], Na^+ and K^+ batteries [59-61] and other fields are widely used. At present, the research on MXene mainly stays on the MXene material itself or the combination of MXene and other materials. With the development of MXene research, researchers are no longer satisfied with this, but to further develop and study MXene. With the efforts of researchers, the research focus of MXene- has gradually shifted to MXene derivatives [18, 62]. MXene derivatives, with their excellent electrochemical and mechanical properties, are showing a wide range of application prospects in many fields. The MXene derivative $Na_2Ti_3O_7$@C material developed by Xu's team [63], a kind of amorphous carbon coated spheroidal nanoparticles, was used as a negative electrode material in Na^+ batteries. It can be seen from the CV curve that the derivative material has a high degree of reversibility. After 200 cycles, The $Na_2Ti_3O_7$@C electrode can still output a reversible capacity of 119mAh/g, the corresponding capacity retention rate is 93.5%, and the capacity attenuation per cycle is only 0.026%. Thanks to the nano-cross-linked structure of the outer carbon layer and the flocs, the transmission path of Na^+ is shortened, the embedding and exiting of Na^+ is convenient, and the structural stability is increased, thus showing excellent magnification performance and high Coulomb efficiency. There are also teams at MXene that demonstrate the purpose of building heterojunctions to achieve synergistic enhancement[64], For example, Song's team[65] developed a MXene derivative called Ta_4C_3-Ta_2O_5 heterojunction and used it as a bifunctional modified film in Li-S batteries. This heterogeneous structure has efficient chemical anchoring and abundant active sites, which can fix polysulfides through synergistic effects, thus giving Li-S batteries stable long-cycle performance. With an initial high capacity of 801.9mAh/g at a current density of 1C, the capacitance decay rate after 500 cycles is only 0.086%. In addition, based on the interaction of Lewis acid, Li^+ and S^{2-} in Li-S batteries will form strong TA-S and Li-O bonds with Ta ions in Ta_2O_5 on the surface. Due to the influence of its high Young's modulus (up to 384GPa), Ta_4C_3 helps to form a protective layer on the Li metal surface. In order to inhibit the growth of Li dendrites, so as to increase their cycle life. The cross-linked structure in MXene derivatives can optimize the electron conduction path, improve the conductivity of the material, and promote the synergistic effect of different conductive mechanisms Chen's team[66] used this to interconnect carbon fibers with NiFe layered double hydroxides (NiFe LDH)/MXene derivatives for electromagnetic wave absorption. Carbon fiber, as the main dissipative material, provides excellent conductive losses in composites. MXene is derived into TiO_2, and the large sheet feature of $FeNi_3/TiO_2$ is derived from the MXene support, which facilitates the connection between adjacent carbon fibers. In addition, the conductive properties of $FeNi_3/TiO_2$ enable electrons to migrate freely between the fibers and form conductive channels, thus promoting conductive penetration effects and further enhancing the conductive loss of carbon fabrics. The stronger conductive loss can also explain its better absorption properties over other granular materials that mainly rely on weaker polarization losses and magnetic losses. The interconnected carbon fabrics have good impedance matching, allowing maximum entry of incoming electromagnetic waves. The porous character of the fabric may induce multiple scattering, thus enhancing the interaction of the wave absorber. Large $FeNi_3/TiO_2$ sheet structures act as conductive connectors between carbon fibers at osmotic thresholds to achieve significantly enhanced conductive losses for efficient absorption. Another team [67, 68]used MXene derivatives in sensors and catalysts to detect miRNA-27a-3p and hydrogen storage.

The diversity and functional application of MXene derivative materials further prove that MXene as a new material has enough advantages and research space. With the development of research, the scope of application of MXene can be expanded one by one, and it is no longer limited to a single composite material. The successful application of derivatives promotes the further development of MXene materials. It has become one of the hot spots of modern material science research.

4. Summary and Outlook

As representatives of new two-dimensional materials, MXene and its derivatives show broad application potential in energy storage and conversion, electromagnetic shielding, sensing and detection, catalysis and other fields with their unique layered structure, high electrical conductivity, controllable surface chemistry and excellent mechanical properties. Compared with traditional electrode materials, MXene-based materials significantly improve the power density, cycle stability and flexible compatibility of energy storage devices through structural design and functional derivation. For example, MXene-derived heterojunction structures, doped carbon composites, and functionalized modification strategies not only optimize electron transport paths and ion diffusion dynamics, but also achieve multifunctional integration through interface synergies.

However, the current research still faces many challenges: First, the environmental stability of MXene materials has not been completely solved, and its surface functional groups are easily affected by oxidation or hydrolysis, resulting in performance attenuation; Secondly, the large-scale preparation process and cost control still need to be broken through, especially the development of green and low-toxicity etching routes. In addition, the structure-activity relationship of MXene derivatives is still in the exploratory stage, and in-depth understanding of its energy storage mechanism and interface reaction kinetics is the key to further improve performance.

The future development direction can focus on the following aspects: (1) To construct an efficient charge storage interface through atomically accurate regulation of MXene layer spacing, surface functional groups and defect engineering; (2) Develop new composite systems such as MXene with organic frameworks and bio-based materials, and expand its application in the intersection fields of flexible electronics and biomedicine; (3) Combine artificial intelligence and high-throughput computing to accelerate the design and screening of novel MXene derivatives; (4) Promote the integration and miniaturization of MXene-based devices, and realize the deep integration of self-powered systems and intelligent Internet of Things. With the collaborative innovation of materials science and engineering technology, the MXene family is expected to break through the existing bottleneck and become the core pillar of the next generation of high-performance and sustainable energy materials, helping to achieve the strategic goal of "two-carbon".

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