本科毕业论文

Synthesis and electrochemical application of graphene - manganese novel dioxide composite

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Synthesis and electrochemical application of graphene-manganese dioxide novel composite

新型石墨烯-二氧化锰纳米复合材料的制备及其电化学应用

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content

Abstract

The supercapacitor is a new type of energy storage element. Compared with traditional batteries and capacitors, it has better electrochemical performance, cleanness and environmental friendliness, and has great application potential in many fields. Therefore, supercapacitors have attracted more and more attention.

In this paper, we report a quick and simple method to prepare graphene -MnO_2 composite as a new electrode material by microwave irradiation. For this composite material, graphene nanosheets are mainly used as highly conductive carriers, which can also provide a larger specific surface area for depositing MnO_2 particles. Due to the high conductivity of graphene, outstanding interface contact and increased contact area between graphene and MnO_2, conductivity of the electrode can be significantly improved. In addition, due to the high specific surface area of the composite, the electrolyte solution can easily enter the surface of the composite, and the electrochemical utilization efficiency of MnO_2 is improved, which can not only provide high reversible pseudo-capacitance, but also provide excellent capacitance retention. Through SEM, CV and EIS test, it is found that the specific capacitance of the composite is 455 F/g at 1 A/g and 416 F/g at 5 A/g, and the capacitance retention rate is 91.4%, which means excellent electrochemical performance. The enhanced high-rate electrochemical performance is due to the increase of electrode conductivity in the presence of graphene network, effective interface area between MnO_2 and electrolyte and the increased contact area between MnO_2 and graphene.

Key-words: Supercapacitor; Graphene; Manganese dioxide; Microwave assisted synthesis; Composite material

Chapter 1 Introduction

1.1 Introduction

With the rapid development of society, science and technology not only bring people convenience in life, but also make people have to face the problem of energy exhaustion. With the rapid spread of industrialization, the consumption of fossil fuels has increased rapidly, and the reserves have decreased rapidly. Non-renewable fossil fuels, such as oil and coal are already facing depletion[1]. In addition, the following problems, such as greenhouse effect and environmental pollution, make it extremely urgent to find and use new environment-friendly energy, and people begin to urgently find and develop various alternative resources. In this case, new energy sources, such as solar energy, wind energy and tidal energy, are put into use on a large scale. In the meanwhile, some new electronic products, such as new energy vehicles and portable electronic devices, have also been developed and put into the market for people to buy and use. However, the following problem is that the traditional energy storage devices are increasingly unable to meet the requirements of new energy equipment[2]. For example, the energy conversion and storage in the process of wind power generation, the instability of energy output power and the energy cycle and service life requirements of pure electric vehicles. Therefore, it is necessary to develop new energy conversion and storage devices[3].

Supercapacitor is a new energy storage device between traditional capacitor and battery. It has higher energy density than traditional capacitors and higher power density than batteries. Moreover, supercapacitors have the advantages of high safety, long cycle life, low cost and environmental friendliness. Because of these unique properties, supercapacitors have attracted the attention of many researchers and organizations in the field of new energy, and also have broad application and research prospects in the fields of national defense and military, aerospace, transportation, electronic information and instruments and so on, and many commercial applications have been achieved.[1]

1.2 Supercapacitor

1.2.1 Overview of supercapacitors

The concept of supercapacitor originated in 1950s, and was made on the basis of interface electric double-layer theory proposed by Helmholtz (1821 ~ 1894)[2]. It is also called an electrochemical double-layer capacitor, gold capacitor and Faraday capacitor, and it is a new energy storage component between traditional capacitor and battery. Compared with that traditional capacitor, supercapacitors have higher energy density and specific capacity, and are

more green and environmental friendly; Compared with rechargeable batteries, supercapacitors have higher power density, longer cycle life and higher safety, and can realize fast charge and discharge with large current. In the fields of machinery manufacturing and commerce, supercapacitors have become ideal energy storage devices developed and applied on a large scale. With the continuous innovation of electrode materials and the rapid development of manufacturing technology, the industrialization process of supercapacitors is accelerating, and the global market scale is maintaining a high growth rate.

According to its energy storage mechanism, supercapacitors can be divided into pseudo-capacitors and double-layer capacitors. Pseudo-capacitors rely on the chemical reaction between electrode materials and electrolyte to realize energy storage, while electric double-layer capacitors realize charge and discharge due to the movement and accumulation of positive and negative charges in electrolyte.

1.2.2 Electrical double-layer capacitor

Electric double-layer capacitor usually includes four main components: double electrode, electrolyte, current collector and diaphragm. The basic working mechanism of an electric double-layer capacitor is that the two electrodes soaked with electrolyte are separated by a diaphragm in the middle. During charging, the positive and negative charges in the electrolyte rapidly gather on the surfaces of the positive and negative electrodes under the action of the electric field, and a charge layer is formed on the surfaces of the two electrodes and electric double-layer. At this moment, a potential difference is formed between the two electrodes, thus forming a capacitance effect and further realizing energy storage; When discharging, the charges accumulated on the electrode surface return to the electrolyte, thus forming a discharge current in the external circuit.

Because chemical reactions such as oxidation and reduction do not occur in the working process, the electric double-layer capacitor can be charged and discharged quickly, and its cycle life is much longer than that of ordinary batteries, and it will not cause environmental pollution. As an energy storage device, compared with batteries, electric double-layer capacitors have relatively small energy density, but higher power density[15]. The advantages are obvious. In addition, the electric double-layer capacitor has the outstanding advantages of wide working temperature range and low maintenance cost.

With regard to the selection of electrode materials, carbon materials are favored by research and application fields because of their high conductivity, large specific surface area,

good stability and wide potential window. Among them, porous carbon materials have a larger specific surface area and atomic-scale charge spacing. Therefore, using porous carbon as electrode material can make the electric double-layer capacitor obtain relatively higher capacitance. At present, carbon materials that are researched and applied in the field of supercapacitors mainly include activated carbon, graphene, carbon nanotubes, and expanded carbon fibers and so on. Different carbon material has different forms, physicochemical properties and electrochemical energy storage properties.

1.2.3 Pseudo-capacitor

Pseudo-capacitor, also known as Faraday capacitor, its basic energy storage mechanism is: Pseudo-capacitor mainly uses metal oxide or conductive polymer as electrode material. When charging, the capacitance of the pseudo-capacitor mainly comes from the rapid and reversible oxidation-reduction reaction of electrode materials, which makes the potential difference between the two electrodes and forms the pseudo-capacitance effect. While discharging, the two electrodes will react inversely to the charging process, thus reducing the potential difference between the two electrodes and realizing the release of energy. In a word, pseudo-capacitors store energy through internal rapid and reversible chemical reactions.

Because the charge accumulation of electric double-layer capacitor only occurs on the electrode surface, while the charge transfer and storage of Faraday pseudo-capacitor occurs in the two-dimensional body of the whole electrode material, the specific capacity and energy density of pseudo-capacitor are far greater than those of electric double-layer capacitor. In addition, compared with the electrode material of the battery. The electrochemical reaction on the electrode material of pseudo-capacitor is more rapid, which leads to higher power density and better electrochemical performance of pseudo-capacitor.

At present, the research on electrode materials of pseudo-capacitors mainly focuses on many kinds of potential metal oxides, such as ruthenium oxide, cobaltosic oxide, nickel oxide, tungsten oxide, manganese dioxide and so on. Among many metal oxides, manganese dioxide has the advantages of high theoretical capacitance (1370 F/g)[4], wide potential window, safety, non-toxicity, low cost and abundant natural reserves. Therefore, it is considered as an electrode material with the most research value and development prospect. However, supercapacitors using pure manganese dioxide as electrode materials usually have the disadvantages of poor conductivity and low ion diffusion coefficient, which affect the performance of supercapacitors[5]. In order to overcome these shortcomings of manganese dioxide electrode materials, many conductive materials are used as additives to improve the performance of

supercapacitors. These conductive materials usually include graphene, conductive polymers, carbon nanotubes and other substances.

The electrode material composed of manganese dioxide and conductive material has excellent electrochemical performance and flexibility, which enlarges the advantages of manganese dioxide and makes up for its shortcomings. At present, there are three main methods to enhance the electrochemical properties of manganese dioxide electrode materials by modifying their structures:

（1） Growth of MnO_2 on nanometer metal materials with superior electrical conductivity, or growth of nanometer metal particles on MnO_2.

（2） Carbon-based materials are combined with MnO_2 by physical or chemical methods to form composite electrode materials with high performance.

（3） The microstructure of electrode materials is changed by special means, such as changing the particle size of MnO_2 and generating MnO_2 on materials with relatively large specific surface area.

1.2.4 Application prospect of supercapacitors

Supercapacitors are widely used in electronic communication, transportation, aerospace, machinery manufacturing and other fields as a new type of energy storage component because of their outstanding advantages such as high energy density, high power density, high volt-ampere current and long cycle life. In addition, people and organizations in related scientific research fields continue to explore more application possibilities of supercapacitors.

At present, supercapacitors are mainly used as auxiliary power supply, standby power supply, main power supply and alternative power supply to provide and store electric energy for devices.

（1） Auxiliary power supply: it is commonly used in power devices of electric vehicles. Composite power supply composed of supercapacitors and batteries in parallel can make up for the problems of low power density, long charging time and short service life of secondary batteries and fuel cells such as lithium ion batteries, and improve the safety of power supply system[1]. This kind of parallel battery has been widely used in the field of electric vehicle manufacturing, which also makes it possible to popularize electric vehicles.

（2） Backup power supply: At present, supercapacitors are mainly used as backup power supply in electronic products, such as ovens, video recorders, taxi meters, etc.

Supercapacitors are used in electric energy devices of electronic equipment, which can give full play to their characteristics of low cost, good stability, fast charging and discharging speed and long service life.

（3） Main power supply; Because supercapacitors can provide large current pulses instantaneously, electric toys can be charged and reused in a short time if they are used as power supply. Moreover, supercapacitors have extraordinary cycle life, which is more economical than secondary batteries.

（4） Alternative power supply: supercapacitors can be combined with light-emitting diodes and solar cells, and applied to solar watches, solar street lamps, traffic lights and other devices. During the day, the solar cell works as the main power supply and supplies power to the supercapacitor, while at night, the supercapacitor continues to provide electrical energy as the power supply.

1.3 Graphene

1.3.1 Introduction of graphene

Graphene is a single-layer honeycomb crystal formed by the hybridization of carbon atoms through sp^2, and it is also the basic unit of many carbon allotropes, such as graphite, fullerene and carbon nanotubes[7]. The theory of graphene was put forward in 1940, but it was not been made until 2004 that Geim and his colleagues really made single-layer graphene by mechanical stripping. Graphene, as a new member of the carbon material family, has unusual structural characteristics, so it also has many properties that other materials do not have, such as the thinnest known material, good electrical conductivity, high mechanical strength, good light transmission, good thermal conductivity and low thermal deformation coefficient[12].
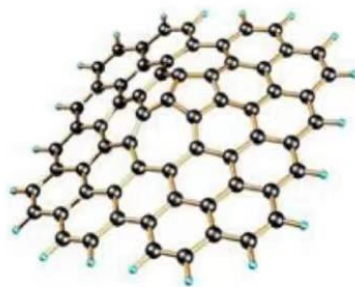

Figure 1. Structure of graphene

1.3.2 Preparation method of graphene

(1) Mechanical stripping method

Mechanical stripping is one of the common methods for preparing monolayer graphene, and Geim et al. prepared monolayer graphene for the first time by this method. According to the method, a single layer of graphene is obtained by repeatedly stripping with a photoresist on the surface of artificial graphite. Its advantages are easy operation and low cost, but there is a certain contingency, which makes it impossible to achieve stable mass production of graphene. In addition, graphene prepared by mechanical stripping method has an irregular shape and low practicability, and cannot be put into commercial production well, which is usually limited to laboratory preparation.

(2) Chemical vapor deposition method (CVD)

Gas-phase precipitation means that carbon-containing gas is treated at high temperature, and a chemical reaction occurs between molecules and atoms, so that carbon element is deposited on the surface of catalytic metal or carbon element incorporated in metal is precipitated on the surface to obtain graphene. According to the solubility of carbon in metals, the former or both coexist in the process of vapor precipitation. Many studies show that, whether there is carbon doping in metals such as nickel, iron, platinum, cobalt, etc., in the process of using CVD, the surplus carbon element precipitated from the metal interior can be treated by special steps to form graphite layer on the metal surface. Graphene prepared by CVD covers the surface of the metal, and how to separate graphene from matrix metal has become a difficult point in its application. However, the graphene prepared by this method is less limited, the number of layers is easy to control, and the production cost is low, so it is a promising preparation method for commercial application.

(3) Thermal decomposition of SiC

Heating SiC at high temperatures makes the surface structure of SiC change. Si atoms are separated from the crystal, and the remaining C atoms on the crystal surface are rearranged and epitaxially grown to form a graphene structure. In the process of pyrolyzing SiC, the structure and properties of graphene depend on the reactor pressure and atmosphere type. For example, when graphene is grown on h-SiC(0001), the number of graphene layers can be well controlled by controlling the external conditions to reach the appropriate standard. SiC method is similar to the CVD method. Graphene is prepared by C atom self-assembly, and the preset graphene structure can be obtained by controlling the matrix material. It is an economical and effective method.

（4） Reduction graphene oxide method

The method of reducing graphene oxide is the most common method for preparing graphene in a laboratory at present, which has the advantages of convenient operation, low

requirements for equipment and batch production. The principle of preparing graphite oxide is to treat graphite with a strong oxidant to oxidize it. Commonly used strong oxidants include potassium permanganate, concentrated nitric acid, perchloric acid and concentrated sulfuric acid. After oxidation treatment, functional groups are inserted between the surface and inner layer of graphite, and the bonding force between graphite layers is weakened correspondingly. Then, graphite sheets with a single layer and low layer number were obtained by reduction.

At present, the main methods for preparing graphite oxide are the Hummers method, Brodie method, Standenmaier method, etc., and the most commonly used method is the Hummers method, because Hummers has the advantages of short oxidation time, high oxygen level, regular product structure and high safety factor. The method is mainly divided into three reaction stages: low temperature, medium temperature and high temperature, and the intercalation of sulfuric acid molecules between graphite layers mainly occurs in the low-temperature process; The deep oxidation of graphite mainly occurs in the middle-temperature process; Hydrolysis of interlayer compounds mainly occurs in the high-temperature process. At present, there are three main methods for the reduction of graphene oxide: physical cracking, chemical reduction and electrochemical reduction. The physical cracking method refers to the rapid vaporization of functional groups of graphite oxide at a temperature as high as 1050℃, thereby cracking the graphite lamellae. Ultrasonically treating the obtained product in an ultrasonic machine with a certain power to separate graphite sheets from each other, thus preparing graphene. The chemical reduction method refers to ultrasonic treatment of graphite oxide to dissolve it, and then adding reducing agent to reduce it into graphene. Common reducing agents include hydroiodic acid, hydrobromic acid and halogen compounds. The electrochemical reduction rule is to precoat graphene oxide on the electrode surface, introduce constant current, and rely on electrochemical effect to reduce graphene oxide quickly and effectively.

（5） Other methods

There are many other methods for the preparation of graphene, but there are few reports and they are not commonly used, such as the arc discharge method.

1.3.3 Physical and chemical properties of graphene

The thickness of graphene is about 0.33nm~1.6nm, and it has a 2D honeycomb single-layer crystal structure connected by sp^2 bond, which is also the thinnest material known at present. However, the fracture strength of graphene is as high as 200 times that of steel, and its Young's modulus and Poisson's ratio are 1.02TPa and 0.149, respectively. Graphene has

some characteristics of semiconductors, its conductivity is 7200S/m at room temperature, the electron mobility reaches 200,000 cm^{2}v/s, and the thermal conductivity of monolayer graphene is 4.84 *10^3~5.30 *10^{3}Wmk^{-1} at room temperature. Graphene is a compound stacked by aromatic rings. There are large π bonds above and below graphene molecules, so it is easy to insert molecules with frontier orbitals. Due to the existence of this electron cloud, electrophilic substitution on its molecule is more likely than nucleophilic substitution, and cyclic addition, insertion reaction and so on can take place on its molecule.

1.4 Manganese dioxide

1.4.1 Brief introduction of manganese dioxide

Compared with carbon materials, metal oxides have higher energy density and better electrochemical stability than conductive polymers. Metal oxides have higher specific capacitance and good cycling performance, so they are considered as electrode materials with research value. Ruthenium dioxide is one of the most studied electrode materials. However, ruthenium dioxide is extremely toxic and expensive, so its application is limited. Therefore, manganese dioxide has attracted people's attention because of its advantages of low cost, no pollution, no toxicity and wide availability of raw materials. According to Faraday's theorem, the theoretical specific capacity of manganese dioxide is as high as 1370 F/g, which has good charge storage performance. It is an ideal electrode material with high-cost performance. In recent years, manganese dioxide has attracted more and more attention from scientific research fields, and its application in lithium batteries and supercapacitors has made great progress.

Manganese dioxide is not bound strictly according to the molecular formula of MnO_2, but generally its molecular formula can be written as MnOx, where X represents the oxygen content in the structure, but the value of X is generally less than 2[9]. The basic skeleton structure of manganese dioxide is [MnO_6] manganese-oxygen octahedron, which takes oxygen atom as
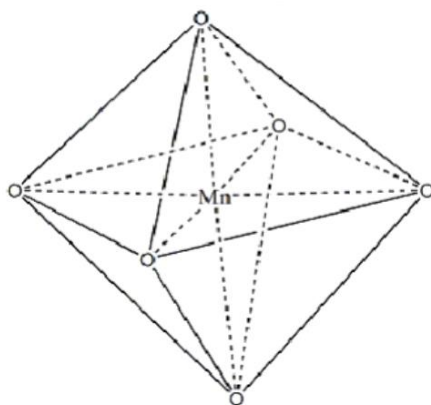
Figure 2. A manganese dioxide unit cell

the vertex of each corner, while manganese atom is located in the center of the octahedron. $[MnO_6]$ is the basic structural unit of manganese dioxide. Its structure is shown in Figure 2.

The chain structure is formed in the way of co-roof and co-edge, and the chain structure is combined in the way of co-roof again to form one-dimensional, two-dimensional and three-dimensional structures, so that manganese dioxide has different space tunnel structures[9]. According to the connection mode of the octahedron in manganese dioxide and the spatial form of an internal tunnel, manganese dioxide can be divided into three types: One-dimensional tunnel structure, two-dimensional layered structure and three-dimensional network structure. One-dimensional tunnel structure mainly includes α, β and γ types. The two-dimensional layered structure includes δ-MnO2. The three-dimensional network structure mainly contains λ-MnO2.

1.4.2 Electrochemical performance of manganese dioxide

Manganese dioxide is a pseudo-capacitor electrode material, which is based on the reversible exchange of protons in electrolyte with manganese on the electrode under the voltage window of the electrode material, and the highly reversible Faraday reaction takes place to obtain a pseudo-capacitor. As mentioned above, manganese dioxide crystal is composed of $[MnO_6]$ octahedral unit cells arranged in order, which are usually mixed crystal structures. Different crystalline states lead to differences in capacitance performance of manganese dioxide, and even manganese dioxide with the same crystalline state has great differences in capacitance performance due to different crystallinity[10].

Generally, there are two ways to store energy in manganese dioxide electrode materials. One is the surface adsorption-desorption mechanism, that is, protons and alkali metal cations in electrolyte are reversibly adsorbed and desorbed on the electrode surface to store and release energy. The reaction mechanism is shown in Formula (1).

$$（MnO_2）_{surface}+M^++e^- \rightleftharpoons （MnO_2·M）_{surface} \quad (1)$$
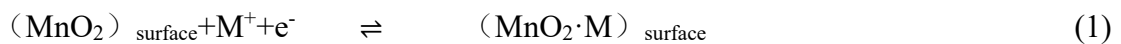
The other is that the protons and alkali metal cations in the electrolyte are intercalated and deintercalated on the surface of the electrode material or inside the material structure, and a rapid and reversible redox reaction occurs to store charges, and the reaction mechanism is shown in Formula (2).

$$MnO_2+M^++e^- \rightleftharpoons MnOOM \quad (2)$$

In which m represents alkali metal cations and protons present in the electrolyte.

The way of storing electricity by manganese dioxide electrode material is realized by the above two ways, in which the electric double-layer capacitance behaviour occurs in the low potential region of scanning voltage, and the pseudo-capacitance behaviour occurs in the high potential region. In the crystalline manganese dioxide crystal, the electrode material mainly undergoes the reaction expressed by formula 2, while in the amorphous manganese dioxide electrode material, A surface reaction represented by formula (1) mainly occurs.

1.4.3 Preparation method of manganese dioxide

Manganese dioxide with different structural types can be prepared by using different preparation methods. At present, the preparation methods of manganese dioxide mainly include the molten salt method, liquid-phase precipitation method, hydrothermal method, sol-gel method, electrochemical precipitation method and so on[8]. Among them, the liquid-phase precipitation method, molten salt method and hydrothermal method all reduce potassium permanganate by using a reducing agent to prepare manganese dioxide powder. However, due to the different reaction environments of these three methods, the structure and composition of manganese dioxide are not completely the same. The products prepared by liquid precipitation method are mainly α-MnO_2, and the products prepared by the molten salt method are mainly mixed crystals of α-MnO_2 and γ-MnO_2 (heating temperature is 450~550°C) or amorphous manganese dioxide (heating temperature is 350°C)[9].The hydrothermal method is a common method for preparing manganese dioxide nanowires, and the crystal form of manganese dioxide can be effectively controlled by controlling reaction conditions. The sol-gel method has two main steps: formation of coordination precursor and high-temperature calcination in an air environment. For example, citric acid and manganese acetate are used to harden hydrogel at 80℃[9]. Then, excess hydrogen and oxygen elements in the product are removed by high-temperature heating to obtain manganese dioxide powder. There are two kinds of electrochemical precipitation methods, one is to oxidize divalent manganese ions by oxidation potential, the other is to reduce permanganate ions by reduction potential. At present, the most commonly used methods in the laboratory are the precipitation method, sol-gel method and hydrothermal method. The electrochemical precipitation method is widely used in industry. Among them, the above-mentioned liquid-phase precipitation method is mature in preparing amorphous manganese dioxide. The preparation of manganese dioxide by liquid-phase precipitation method has the advantages of simple operation, no need of heating, high safety, fast preparation speed, low manufacturing cost and so on[16] In addition, manganese dioxide prepared by liquid phase precipitation method generally has a low degree of

crystallization, and amorphous materials have better electrochemical performance than crystalline materials. At the same time, the liquid precipitate reacts in the liquid phase, and the uniform quality of the product can be ensured by controlling the reaction speed and stirring speed. Generally, manganese dioxide prepare by liquid-phase precipitation is dripped into potassium permanganate solution. At present, known reductants are manganese sulfate, manganese acetate, ethanol, citric acid and so on. If the crystallinity of manganese dioxide is to be improved, the manganese dioxide can be calcined at a high temperature, and the required manganese dioxide powder can be obtained by controlling different calcination temperatures[20].

1.5 Preparation of Graphene/Manganese Dioxide Composite

Composite materials made of manganese dioxide and graphene can complement each other's advantages and obtain electrode materials with superior performance. As the structure and morphology of graphene and manganese dioxide will have a very important influence on the final composite products. Therefore, how to choose the appropriate composite method and how to deal with the matrix material reasonably has become the focus of research. There are mainly hydrothermal method, electrochemical deposition method, chemical vapor deposition method, solution growth method and so on[19].

Hydrothermal method: under the conditions of high temperature and high pressure, metal salts are hydrolyzed and crystallized in a reaction kettle, and the solvent is used as the medium in this process[21]. Nanometer manganese dioxide prepared by the hydrothermal method has the advantages of high purity, small particles, good dispersibility, few structural defects, etc., and the steps are simple and easy to operate.

Electrochemical deposition method: oxidation-reduction reaction of reactants takes place under the action of the electric field, so that products are generated on electrodes. Electrodeposition has the advantage of simple operation.

Chemical vapor deposition (CVD): chemical gas or steam reacts on the surface of the substrate to form a coating. The carbon material prepared by this method has a high graphitization degree, good crystallinity and excellent mechanical properties, which is beneficial to the transfer of electrons in the working process of the electrode, but the cost is high.

Solution growth method: α-MnO_2 nanofibers were synthesized on three-dimensional graphene by using $MnSO_4$ and ammonium persulfate as oxidants.

1.6 Microwave synthesis technology

Microwave-assisted synthesis is a relatively new preparation method of nano-materials in recent years. Its principle is that polar molecules in substances rotate and rub rapidly and repeatedly in the alternating electric field applied by microwave generator, so as to generate a thermal effect, which makes polar molecules heated uniformly, thus rapidly crystallizing and obtaining nano-materials with uniform particle size[11]. Compared with the traditional heating treatment,microwave-assisted synthesis technology has the advantages of fast heating speed, uniform heating of molecules, high efficiency, energy saving, environmental friendliness and selective heating[8].

1.7 The significance and research contents of the paper

1.7.1 The significance of the paper

With the development of science and technology, people's demand for energy is increasing, and because of the heavy dependence of industry and life on gasoline, coal and other energy sources, the environmental pollution and greenhouse effect of the earth is becoming more and more serious. Many fossil energy sources are also facing depletion, so people turn their attention to the new energy field. Since the 1990s, the research on supercapacitors has gradually arisen. Although supercapacitors have good energy storage performance and have good development potential in the fields of solar cells, electric vehicles, power conversion devices, etc., their low energy density, high manufacturing cost and lack of industry standards limit their application. At present, the research on supercapacitors is mainly to develop a kind of supercapacitor with low cost, electrode materials with high specific capacity can be accepted by the traditional energy market.

Since graphene was first discovered in 2004, it has been found to have excellent properties such as large specific surface area, high mechanical strength, strong electrical conductivity and good chemical stability[17]. However, graphene also has many shortcomings that cannot be ignored, such as high manufacturing cost, which is also the main problem that limits the wide application of graphene[18]. In addition, if pure graphene is used as the electrode material, the electrode has low specific capacitance and does not have excellent electrochemical performance, so it is a feasible solution to use graphene as the carrier of other materials to make composite materials. Manganese dioxide is a common electrode material for zinc-manganese batteries, which has the advantages of low cost and high theoretical specific capacity. While the ideal MnO_2 has excellent performance, however, there are still many defects in its application state, the most restrictive of which is that its conductivity is not high, which leads to the inability to transfer electrons efficiently when manganese dioxide is

used as an electrode, thus making the utilization rate of manganese dioxide extremely low[8]. If graphene and manganese dioxide are compounded, the advantages of graphene and manganese dioxide can be fully utilized, and each other's shortcomings can be overcome, which has high research value.

1.7.2 The research contents of the paper

1. Study the preparation method of graphene

Graphite oxide (GO) was prepared by Hummers method, and graphene oxide was reduced by the chemical reduction method. The surface structure and electrochemical properties of graphene were characterized, and the effects of treatment time in chemical reduction and hydrazine hydrate treatment on graphene structure were studied.

2. Microwave-assisted preparation of graphene/manganese dioxide composites and their electrochemical properties were studied. In the microwave reaction environment at normal pressure, a set of parameter combinations with the best performance of electrode materials were prepared and selected by controlling a series of reaction parameters such as reaction temperature and reaction time. Under this set of reaction parameters, composite electrode materials were prepared. The reasons for the improvement of electrochemical performance were analyzed.

Chapter 2 Experiment

2.1 Experimental materials and equipment

Table 1 Experimental reagents and raw materials

reagent	Model/specification	manufacturer
natural graphite	450 mesh	Shanghai Yifan graphite co., ltd
potassium permanganate	analytical grade	Beijing Yili fine chemicals co., ltd
concentrated sulfuric acid	98%, analytical grade	Beijing Yili fine chemicals co., ltd
phosphoric acid	analytical grade	Tianjin Hengxing chemical reagent manufacturing co., ltd
hydrogen peroxide solution	30%, analytically pure	Tianjin Hengxing chemical reagent manufacturing co., ltd
muriatic acid	analytical grade	Beijing Yili fine chemicals co., ltd
carbon black	analytical grade	Xi'an Hongxin chemical industry co., ltd
PVDF	100%	Guangzhou Xingsheng technology co., ltd
hydrazine hydrate	analytical grade	Beijing chemicals factory

Table 2 Test Equipment

reagent	model	manufacturer
Electrochemical workstation	CHI760E	Shanghai Chenhua co., ltd

Scanning electron microscope	JSM-7001F	Japan Electronics Co., Ltd. (JEOL)
Ultrasonic cleaning instrument	KH-100DDB	Kunshan Hechuang ultrasound instrument co., ltd
Microwave oven	MZQ-2070EGCZ	Qingdao Haier Group
Tablet machine	769YP-15A	Tianjin Shikeqi High-tech Company
Ball miller	YXQM-20L	Changsha Miqi Instrument Equipment co., ltd

2.2 Preparation of electrode materials

2.2.1 Preparation of graphene

Firstly, graphite oxide (GO) was prepared by the modified Hummers method. The prepared GO was suspended in water to obtain a brown dispersion, which was dialyzed to completely remove residual salts and acids. The purified GO suspension was then dispersed in water to produce a dispersion of 0.05 wt%. And then ultrasonic treatment is carried out on the dispersion by using ultrasonic waves to realize the peeling of GO. Next, GO was chemically converted into graphene. the obtained uniform dispersion (100 mL), 100 mL water and 2 mL hydrazine hydrate solution (20 wt%) were added into a 250 mL round-bottom mixing flask, and the pH of the suspension was adjusted to 10 with sodium hydroxide solution, and then refluxed at 100°C for 24 hours. Finally, the solid was filtered, washed several times with distilled water and alcohol, and then dried in a vacuum oven at 100°C for 12 hours.

2.2.1 Synthesis of graphene -MnO_2 composite materials

Graphene /MnO2 composites were prepared by oxidation-reduction reaction of graphene and potassium permanganate under microwave irradiation. At first, 100 mL graphene suspension was ultrasonicated for 1 h. Then, 0.08 g $KMnO_4$ powder was added to the graphene suspension and stirred for 10 minutes. Subsequently, the obtained suspension was heated for 5 minutes using a domestic microwave oven, and then naturally cooled to room temperature. Finally, the black precipitate was filtered, washed several times with distilled water and alcohol, and dried in a vacuum oven at 100°C for 12 hours. The mass percentage of MnO_2 in the composite was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, ICPS-7500), and the percentage of MnO_2 in the composite was 20wt%.

2.3 Preparation of electrodes

The working electrode was prepared as follows

（1） The material prepared above, carbon black and conductive binder PVDF were mixed in a mass ratio of 80:10:10 and ground for 2h by a ball miller, so that the mixture was fully dispersed in NMP.

（2） However, the obtained mixture was coated on a nickel foam substrate (1cm×1cm) with a scraper, and then dried in a vacuum furnace at 60°C for 12 h.

（3） Use a tablet machine for tabletting. The loading mass of each electrode is about 5mg.

2.4 Characterization method and principle of material structure image and electrochemical performance

2.4.1 Scanning electron microscope

In this experiment, jsm-7001f scanning electron microscope was used to analyze the micro morphology and surface structure of the materials.

Sample preparation steps: firstly, the sample is evenly dispersed in water or absolute ethanol, and then ultrasonic treatment is carried out for 20 min. Then, a small amount of sample solution is sucked onto the prepared silicon wafer with a dropper, and placed until the solution is completely evaporated. Then, the silicon wafer is glued to the stage of scanning electron microscope with conductive adhesive for SEM test.

2.4.2 Cyclic voltammetry test and its principle

Cyclic voltammetry (CV) is an experimental method in electrochemical research: select a point range, and conduct cyclic voltammetry scanning on the electrode, and record the elegant change of current with scanning, so as to obtain the corresponding curve of current and voltage. According to the peak current and peak potential of the scanning curve, it can be known that within the scanning point range, the electrochemical reactions of electrode materials, the difficulty and reversibility of electrode reactions, the hydrogen evolution characteristics of the electrode, the adsorption / desorption characteristics of the electrode to ions, and the charge-discharge efficiency are discussed.

During the performance test of the supercapacitor, it is assumed that the scanning signal is firstly scanned to the cathode, and the active substance as the electrode material reacts with reduction, then the latter half is scanned to the anode direction, and the reduction product is oxidized again to form a cycle, while the electrode material has no obvious structural change. The parameters that can be controlled in cyclic voltammetry test include scan elegant window,

scan rate and cycle times. By changing the above parameters, the rate performance, specific capacitance performance and cycle stability of the electrode materials can be observed and summarized.

If the test object is an ideal capacitor, the corresponding positive and negative current values should also be changed when the scanning direction is changed. The current signal diagram keeps an ideal rectangle and does not change with the scanning rate. The ideal capacitor does not have internal resistance, but super capacitor in actual measurement has a certain internal resistance. The current cannot be changed into a constant current instantaneously, but gradually changes over a period of time, so that a radian will be formed in the actual test current signal diagram. The shorter the transition time is, the closer the current curve is to the rectangle, which indicates that the smaller the internal resistance of the electrode material is, the closer it is to the ideal capacitor.

2.4.3 Constant current test and its principle

The constant current charge-discharge test is a commonly used method to study electrochemical capacitors. It is to apply a specific charge and discharge current to the tested electrode, study the change of de potential age time, observe its change trend, and study the specific capacitance and equivalent series resistance (ESR) of the electrode

For the discharge test, the specific capacitance of the material can be calculated by the formula (3).

$$C_s = \frac{it_d}{m_\triangle v} \tag{3}$$

In formula (3), the following is true:

i refers to the discharge current, m refers to the mass of electrode active material (g); t refers to the time change of charge or discharge; ΔV refers to the average voltage change.

In the process of the experiment, the charge and discharge performance of the electrode is tested by changing the charge and discharge current. According to the charge and discharge time of the electrode, the specific capacitance of the electrode under different current densities can be calculated, and its power characteristics can be analyzed.If the specific capacity of the electrode remains stable and does not decay when the charge-discharge current increases gradually,it shows that the material has good power characteristics and is suitable for high power charge and discharge.On the contrary, it indicates that the material has poor power characteristics.

2.4.4 Electrochemical impedance test and its principle

Electrochemical impedance spectroscopy (EIS) is an important method to study the

impedance of supercapacitors. The existence of internal resistance in supercapacitor will lead to the decrease of voltage range that can be stored in the capacitor, resulting in the decrease of electrode storage capacity and specific capacitance. The specific capacitance of the electrode is directly related to the voltage window (V).

Cyclic voltammetry (CV), constant current charge-discharge and electrochemical impedance spectroscopy (EIS) were measured by ChI 760E electrochemical workstation.CV tests were performed at different scan rates in the range of 0 ~ 0.8 V (vs. Ag/AgCl).Constant current charge / discharge curves were measured at different current densities in the potential range of 0 ~ 0.8 V (vs. Ag/AgCl), and EIS measurements were performed in the frequency range of 100 kHz to 0.1 Hz with an alternating current amplitude of 5 mV. In the process of testing, three-electrode system was used. Nickel foam coated with graphene or graphene-MnO_2 composite was used as working electrode, platinum electrode and Ag / AgCl were used as counter electrode and reference electrode respectively.

Chapter 3 Results and discussion

3.1 Morphology analysis of graphene / manganese dioxide composite

The microstructure images of graphene and graphene-MnO_2 composites are shown in Figure 3.The graphene after go reduction has wrinkles and creases (Figure. 3a).After the redox reaction between carbon and $KMnO_4$ by microwave irradiation, it can be seen that MnO_2 particles are dispersed on the surface of graphene (Figure. 3b).Many oxygen-containing functional groups (epoxides, hydroxyl groups, etc.) remain on the edge of graphene, carbonyl and carboxyl) are easy to oxidize, and the direct electron transfer from the defect to MnO_4^- will lead to MnO_2 precipitation near the defect site.
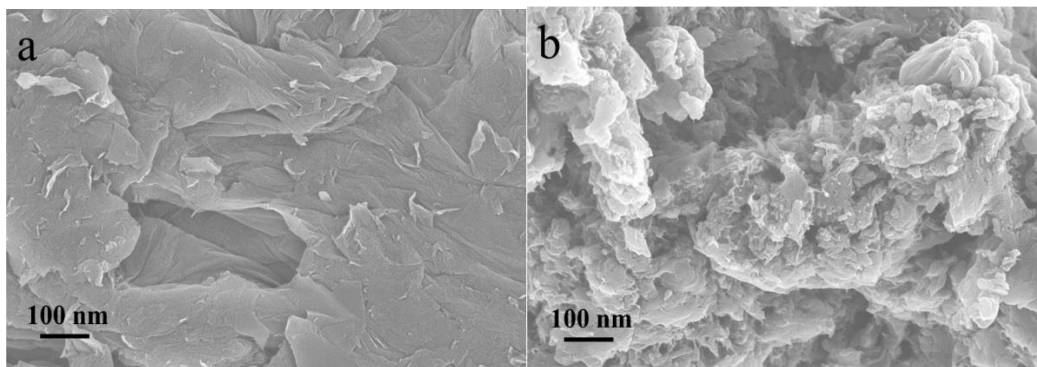

Figure 3. SEM pictures of graphene and graphene MnO_2 composites

3.2 Electrochemical performance analysis of graphene/manganese dioxide composite
3.2.1 Cyclic voltammetry of graphene

The cyclic voltammetry curve of graphene is shown in Figure 4. With the increase of the scanning rate of CV, the shape of CV contour remains relatively rectangular without obvious deformation, showing excellent high rate performance. The results show that the graphene
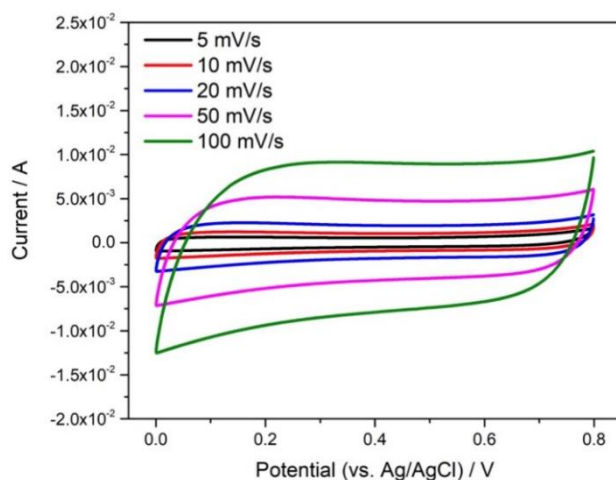

Figure 4. CV curve of graphene

prepared by us has good conductivity.

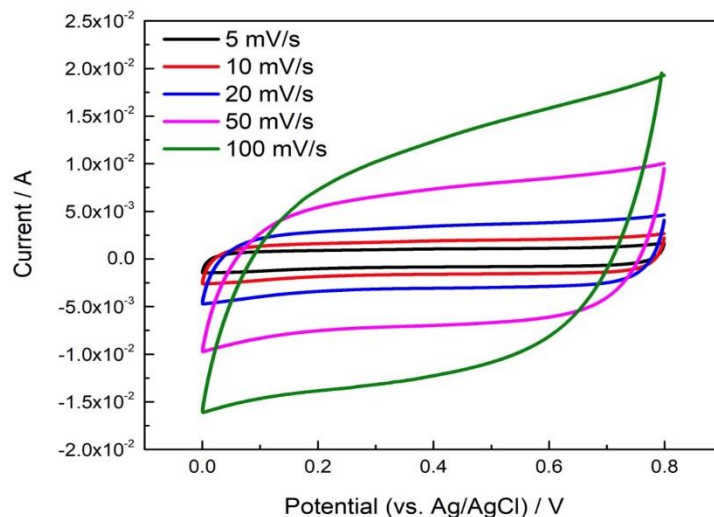## 3.2.2 Cyclic voltammetry of graphene /MnO_2 composite

Figure 5.CV curve of graphene- MnO_2 composites

In the case of graphene – 20% MnO_2 composites, with the increase of CV scanning rate, the contour of CV curve is close to rectangle without obvious deformation. Moreover, there is no obvious redox peak, which indicates that the composite has ideal capacitance performance.

In the previous reports, the CV curve of graphene-MnO_2 composites usually showed a large distortion at the scanning rate of 50 mV / s, but in our study, the CV Curve of graphene-MnO_2 composites did not showed the same change. As shown in the figure, it still maintains the relative rectangular shape, showing excellent high rate performance. The excellent electrochemical performance of graphene-MnO_2 composite can be attributed to its unique microstructure, as shown in Figure 3: (1) MnO_2 particles coated on graphene surface can be accumulated to form ion buffer reservoir pores to improve the diffusion rate of electrolyte ions in the prepared materials; (2) MnO_2 particles can greatly reduce the diffusion length of Na^+ which must be transferred in the process of charge/discharge, so as to improve the electrochemical utilization of MnO_2, and graphene in the composite plays an inhibitory role. Graphene is not only the carrier of MnO_2 particles deposition, but also the electron conduction channel. Moreover, the excellent interface contact between MnO2 and graphene is helpful for the rapid transport of electrons in the whole electrode matrix.

3.2.3 Comparison of cyclic voltammetry between graphene and graphene /MnO_2 composites

Graphene and graphene-MnO_2 composites were prepared at step 1. The CV Curve of scanning rate in mol/L Na_2SO_4 aqueous 2solution at 20 mV/s is shown in Figure 6. There was no obvious redox peak in the CV curves of the two materials. However, at the same scanning rate, the area enclosed by CV curve of graphene-MnO_2 composite is significantly larger than that of graphene, and the results show that the capacitance of graphene-MnO_2 composite is better than that of graphene without MnO_2.
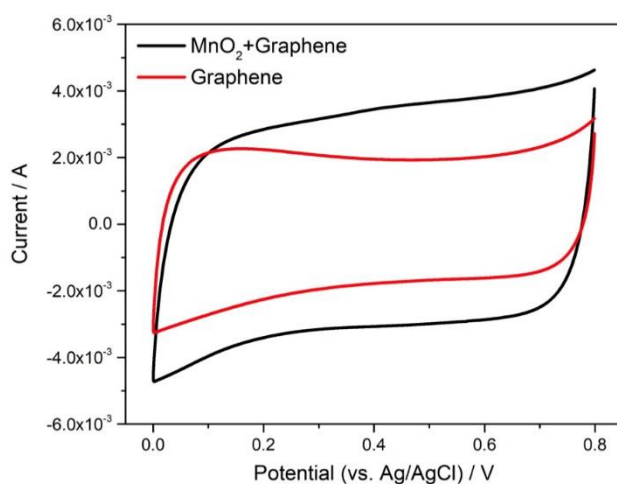

Figuration 6. Comparison of CV curves of graphene and graphene - MnO_2 composites

3.2.4 comparison of constant current charge discharge test between graphene and graphene/MnO$_2$ composite

The GCD curves of graphene and graphene-MnO$_2$ composites in 1 mol/L Na$_2$SO$_4$ aqueous solution at a current density of 1 A/g are shown in Figure 7. The discharge time of graphene-MnO$_2$ composite electrode was significantly longer than that of the graphene electrode. The specific capacitance of graphene-MnO$_2$ composite at 1 A/g is 455 F/g. Under the same conditions, the graphene is 225 F/g. After compounding with MnO$_2$, the specific capacitance of graphene is doubled.
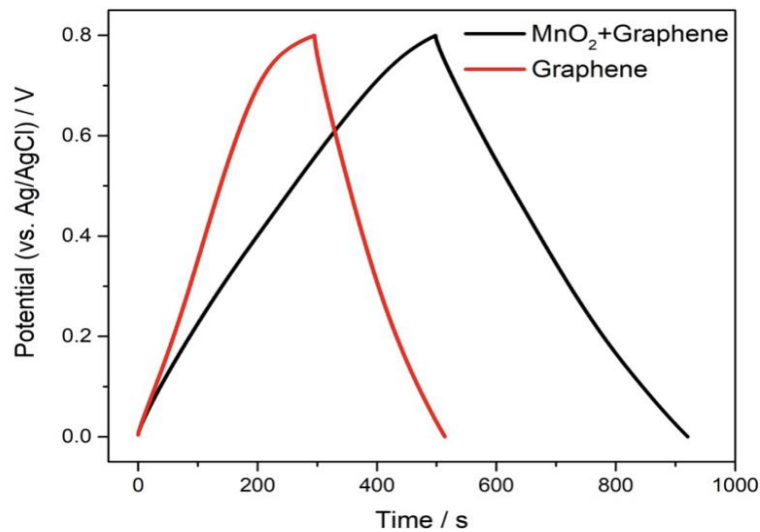

Figure 7. Constant current charge-discharge curves of graphene and graphene MnO$_2$

3.2.5 Constant current charge-discharge test of graphene MnO$_2$

As shown in Figure 8, when the current density is 5 A/g, the specific capacitance is 416 F/g. At the same time, after 10000 charge-discharge cycles, the specific capacitance retention rate of the material is 91.4%. It shows that the electrode material has a good rate performance. The electrochemical performance of the electrode material has been improved obviously because of the increase of the electrode conductivity in the presence of the graphene network. The effective interface area between MnO_2 and electrolyte and the contact area between MnO_2 and graphene increased.
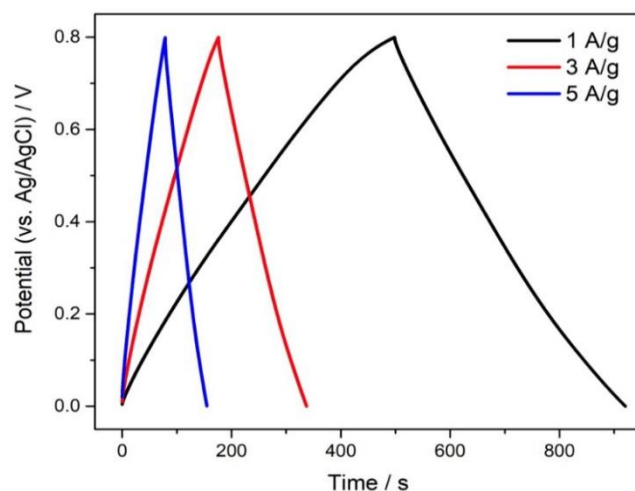

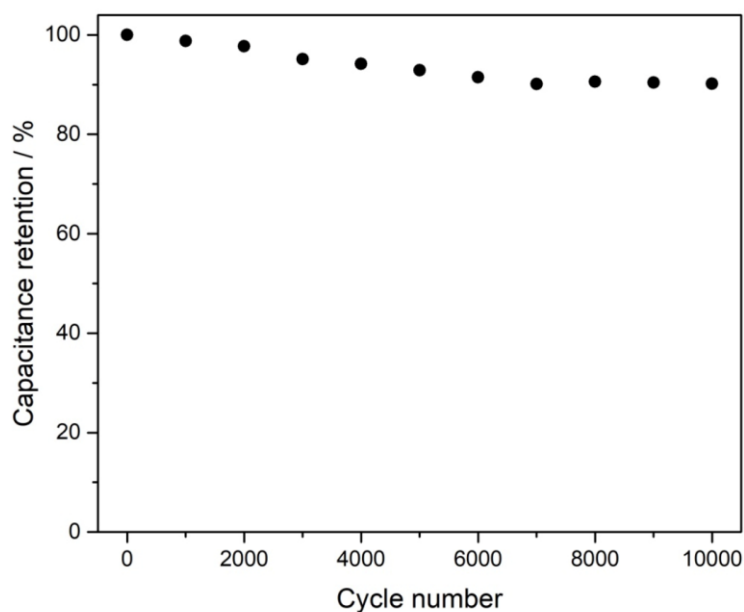Figure 8. Constant current charge-discharge curves of graphene – MnO_2 composites

Figure 9. Specific capacitance retention of graphene/MnO_2 composites

3.2.6 Electrochemical impedance spectroscopy of graphene/MnO_2 composite

Figure 10 shows the impedance characterization of graphene/manganese dioxide composites. The radian of the electrochemical impedance spectroscopy curve of the material
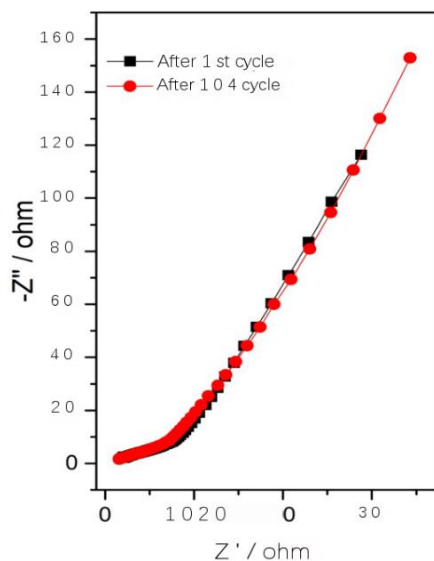

Figure 10. EIS curves of graphene – MnO$_2$ composite

after 10000 current cycles is almost the same as that of the first one, which indicates that the internal resistance of the electrode material has not changed obviously after many cycles and the electrochemical performance is better.

3.3 Summary of this chapter

1. Graphene prepared by modified Hummers method has excellent rate performance and good conductivity in cyclic voltammetry test.

2. Graphene -MnO$_2$composites prepared from the above materials show ideal capacitance performance in a series of electrochemical characterization. When the current density is 5 A/g, the specific capacitance can reach 416 F/g, the capacitance retention rate is 91.4% higher, and the internal resistance remains almost unchanged after many cycles.

Chapter 4 Conclusion

In this paper, graphene /MnO_2 nanocomposite with excellent capacitance performance was prepared, and the electrochemical performance of manganese dioxide was improved by doping carbon materials. Graphite oxide was prepared by modified hummers method, and graphene/MnO_2 composite was prepared by microwave irradiation as a new electrode material, which enhanced the supercapacitor performance of manganese oxide-based electrode material. The conclusions of this paper are as follows:

(1) In the above composite materials, graphene has a large specific surface area, which can precipitate more manganese dioxide particles. In addition, graphene has a high electrical conductivity, which makes the prepared electrode materials have good electrical conductivity.

(2) Graphene/MnO_2 composite material has a large specific surface area, which makes electrolyte solution easily enter the material for reversible chemical reaction, and improves the electrochemical utilization efficiency of MnO_2, which can not only provide high reversible pseudo-capacitance, but also provide excellent capacitance retention.

(3) The experimental results show that the specific capacitance of the composite material is 455 F/g at 1 A/g and 416 F/g at 5 A/g, and the capacitance retention rate is 91.4%. The enhanced high-rate electrochemical performance is due to the increase of electrode conductivity, effective interface area between MnO_2 and electrolyte and the contact area between MnO_2 and graphene in the presence of graphene network.

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