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Electrochemical preparation and analysis of organic composites

有机复合材料的电化学制备与分析

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Abstract in English

Using different concentrations of aniline (PA) and γ-Fe_2O_3, by electrocatalytic polymerization method to form composite materials, which can be used in the development of supercapacitor electrode materials. And the composite products were tested to find the best ratio and compare properties of the composites with those of polyaniline. In this experiment, the concentration gradient method was used to design the concentration ratio of aniline (PA) and γ-Fe_2O_3 (1:1, 1:2, 1:4, 1:8, 1:16, 1: 32), and different concentrations of aniline (PA) (50 mM PA was diluted to 50mL with 0.01M, 0.1M and 1M sulfuric acid, respectively), and glassy carbon and uniaxial conductive glass (ITO) were used as working electrodes for comparative experiments, and the synthesis of electrode materials and performance analysis were carried out by cyclic voltammetry. The results show that the ratio of different concentrations has a great impact on the yield and performance of the product. According to the experimental results, in different variables, ITO glass as the working electrode, aniline (PA) diluted with 1M concentrated sulfuric acid, and PA and γ-Fe_20_3 concentration ratio of 4:1 when the synthesis of combined efficiency is the best. The properties of the synthesized compound are much better than those of polyaniline

Key words: supercapacitor; Aniline; γ-Fe_20_3; composite

Abstract in Chinese

使用不同浓度的苯胺（PA）（50 mMPA 分别用浓度为 0.01M、0.1M、1M 的硫酸进行稀释，稀释至 50ml）与γ-Fe_2O_3,以电催化的方法进行聚合形成复合材料，开发可用于超级电容器的材料。并对合成的产品进行检测，找到最佳的合成配比。本实验采用浓度梯度法设计了苯胺（PA）与γ-Fe_2O_3的浓度配比（分别为 1：1，1：2，1：4，1：8，1：16，1：32），以及不同的苯胺（PA）浓度（50 mMPA 分别用浓度为 0.01M、0.1M、1M 的硫酸进行稀释，稀释至 50ml），并且分别采用了玻碳和单向导电玻璃(ITO)作为工作电极进行对比实验，并使用循环伏安法进行电极材料的合成以及性能分析。结果表明，不同浓度的配比对于产物的产量以及性能有很大的影响，就实验结果来看，在不同的变量中，以 ITO 玻璃为工作电极，苯胺（PA）以 1M 的浓硫酸进行稀释，且 PA 与γ-Fe_2O_3的浓度配比为 4：1 时合成的材料效果最好。

关键词：超级电容器；苯胺；γ-Fe_2O_3；复合

Chapter 1 introduction

1.1 Research and development of capacitors

Different capacitors have different ways of electrode materials, dielectric materials, and processing. With the development of the times, different materials and processing methods have worked out the different capacitor, the capacitor research also from paper condenser, aluminum electrolytic capacitors, film capacitors, ceramic capacitors and developed on the basis of the monolithic capacitor to the super capacitor.

Paper capacitor

Paper capacitor is made of two pieces of metal foil (tin foil or aluminum foil) as the electrode, and then sandwiched between two layers of metal foil with extremely thin capacitor paper, rolled them together into cylindrical or flat cylindrical core, and then sealed in the metal shell or insulating material (such as ceramic, glass glaze, etc.) shell made of. It is the oldest type of organic dielectric capacitor. Paper capacitors with different capacitance sizes can be made by changing the area of tin foil or aluminum foil. It has the advantages of low cost, good stability and so on, but the loss is larger. Mainly used in low frequency, high voltage circuit for bypass, coupling, filtering, pulse, phase shift, energy storage and other purposes. With the development of the technology, metallized paper capacitors began to be used gradually, which covered the capacitor paper with a metal film instead of metal foil. In this way, the improved capacitor has a self-healing effect and can continue to work when the voltage is restored to normal after being broken down. The main principle is that after the breakdown of ordinary paper capacitor, the paper medium will be burnt to form a hole, and the two melted plates will contact in the hole and cause the capacitor to fail. However, if the plate material is made of metal film instead of metal foil, the metal film will quickly evaporate at the point of breakdown, leaving only small holes in the insulation, thus ensuring the normal operation of the capacitor. Metallized paper capacitor has high voltage resistance, low loss and low inductance. It can be used in high frequency circuits, suitable for igniters, energy saving lamps, chargers, ozone generators and other DC pulsation circuits.

Aluminum Electrolyte Capacitor (0.47-10000μF)

The electrode plate of this kind of capacitor is aluminum foil, and between the plates there is absorbent paper soaked in paste electrolyte. The electrode plate and absorbent paper are rolled together. The aluminum foil of the positive electrode plate is treated by direct current voltage to form a layer of oxide film, which acts as the dielectric of the capacitor. Aluminum electrolytic capacitors are polar because of the unidirectional conductivity of the oxide film. This kind of capacitor has the advantage of small size and capacity is bigger, so it can withstand large current ripple, and this kind of capacitor in the working process of the oxide film defects repair medium point, has the character of "selfheal", in addition, the capacitor can withstand high electric field strength, about 600 kV/mm, especially suitable for miniaturization and large capacity of the capacitor. The disadvantages of this capacitor are also obvious: because it is made in a more extensive way, its capacity error will be much larger than other types of capacitors, and it will leak current, so it cannot be used in high frequency alternating current and low temperature, and its life is limited, so it cannot be used as a precision electronic component. It is mainly used for renewable energy and stepless variable speed rotation. For example, it is used to absorb the sub-harmonic current with high switching frequency generated by the inverter and the three-fold frequency current and high-order harmonic current of the output frequency.

Film Capacitor (40PF-4μF)

Film capacitors are made of metal foil as the electrode, which is overlapped with plastic films such as polyethylene ester, polypropylene, polystyrene or polycarbonate at both ends and then wound into a cylindrical capacitor. Typically, thin-film capacitors are made by using foil, such as aluminum, as electrodes, and winding together a plastic film. But another method for making thin-film capacitors is called metallized film, in which a thin layer of metal is vacuum evaporated on top of a plastic film to serve as an electrode.[1] In this way, the thickness of the electrode foil can be eliminated and the volume per unit capacity of the capacitor can be reduced, so it is easier to make the film capacitor into a small volume and large-capacity capacitor. The advantage of this kind of capacitor is with low loss of plastic material such as polyester, polystyrene do better medium frequency characteristic, and dielectric loss is small, can ensure that the signal in the process of transmission will not have too big distortion happens, absorbing ability is good, there is no polarity, high insulation resistance and the disadvantage is that the larger kind thin film capacity cannot be made, and because it is plastic film also some poor heat resistance. According to the type of plastic film, this kind of capacitor can be divided into three types: polyethylene ester capacitor (Mylar capacitor), polypropylene capacitor (PP capacitor), polyphenylene capacitor (PS capacitor) and polycarbonate capacitor. Among them, polypropylene (PP) capacitor and polystyrene (PS) capacitor characteristics are the most significant, with good signal transmission performance, is often used in the major audio equipment. In addition, thin-film capacitors have been applied in many industries, such as communication, electric power, electrified railway, hybrid electric vehicle, wind power generation, solar power generation, etc., and are competing strongly with aluminum electrolyte capacitors.

Ceramic capacitor

With the further development of the electronics industry, people demand for capacitor to further improve, and compared with other capacitor dielectric materials, dielectric ceramics has the following characteristics: (1) ceramic materials as synthetic material, ceramic raw materials can be achieved by adjusting control of ceramic medium temperature coefficient of dielectric constant, dielectric constant, mechanical properties and thermal physical properties. (2) The dielectric constant energy of some dielectric ceramics varies with the electric field intensity. This characteristic can be used to manufacture capacitors which can deal with the nonlinear changes of external influences, such as varistor capacitors. (3) The raw materials of ceramics are easy to use and have the characteristics of low cost and mass production. [2] Ceramic capacitors can be divided into two categories: low frequency ceramic capacitors (CT) and high frequency ceramic capacitors (CC) because of their different ceramic materials and properties.

Low Frequency Ceramic Capacitor (10PF-4.7μF)

Low frequency ceramic capacitors have large capacity and low cost, but their capacity is unstable and their loss is large. They are widely used in the situations where the capacity stability and loss are not required high, such as some low frequency and low voltage circuits. Such as ferroelectric ceramics, it has a high dielectric constant, in a certain temperature range can spontaneously polarization, is a kind of ferroelectric body, suitable for the production of capacitors of large capacity, and it has the pyroelectric property so can be made of infrared detectors. In addition, there is a transparent ferroelectric ceramic material, the use of its optical effect can be made of light regulators, laser goggles and other products.

High frequency ceramic capacitor (capacitance: 1-6800pF)

High frequency ceramic capacitor has low dielectric loss and high stability, small size, its capacitance is almost not affected by time, AC signal, DC signal, the temperature coefficient of dielectric constant range is very wide, can vary from a large negative value to a large positive value. Therefore, some ceramics with large negative permittivity temperature coefficients can be used in oscillating circuits to keep the oscillation frequency constant or change very little; In addition, the absolute value of the temperature coefficient of the dielectric constant of some ceramics is very small and has a high stability. In recent years, they have been used in electron microscope, photocopier, space, navigation, missiles and other precision electronic instruments and equipment, and have a good application prospect.

Monolithic Capacitor (10pF~10μF)

Monolithic capacitors, also known as multilayer ceramic capacitors (MLCC), are the most widely used chip components, which combine the inner electrode material and the ceramic body in parallel by alternating layers to form a whole. Therefore, the structure of multilayer chip ceramic capacitor mainly includes three parts: ceramic medium, metal inner electrode and metal outer electrode. Because this kind of capacitor is a multi-layer superimposed structure, it can be regarded as the joint of several simple parallel plate capacitors according to the theory of parallel capacitor superposition. This kind of capacitor has the characteristics of small size, high specific volume and good precision. And this kind of capacitor electrical performance is the most stable, basically does not change with the temperature, voltage, time, belongs to the ultra-stable, low loss capacitor material type, suitable for high frequency, ultra-high frequency, very high frequency circuit which requires high stability and reliability. In recent years, with the improvement of the reliability and integration of chip capacitor products, the application range of this kind of capacitor is more and more extensive. At present, it is mostly used in computers, electronic communication equipment, radar communication, precision test instruments, small electronic equipment and so on.

supercapacitor

The accurate name of supercapacitor is chemical or double electric capacitor (EDLC), a new electronic component, emerged in the 1970s to 1980s, in the United States, Japan, Russia and other countries have a relatively advanced research progress. Supercapacitor is an electrochemical component that stores energy without chemical reactions, so the energy storage process is reversible. It can be seen from this that supercapacitor can be regarded as a combination of traditional capacitor and battery, so it has some characteristics of capacitor and battery. Its main features are: (1) fast charging speed, charging 10 seconds to 10 minutes can reach more than 95% of its rated capacity. (2) Long cycle service life, deep charge and discharge cycle times up to 10-100,000 times, no "memory effect”. (3) High current discharge capacity is super strong, high energy conversion efficiency, small process loss, high current energy cycle efficiency is equal or greater than 90%. (4) High power density, up to 300W/KG~5000W/KG, equivalent to 10-100 times of the battery. (5) The composition, production, use, storage and disassembly of the raw materials of the products are pollution-free, and it is an ideal green and environmentally friendly power source. (6) Charging and discharging circuit is simple, no need to charge the battery as charging circuit, high safety factor. (7) Have good characteristic in ultra-low temperature, the temperature range is wide -40℃ ～+85℃; (8) Capacity range is usually 0.1F--1000F; (9) Supercapacitors have internal resistance and can be charged without load resistance. (10) It has a large storage capacity and can release more current. [3]

Supercapacitors also have some disadvantages: (1) electrolyte leakage can occur if not used properly. (2) Supercapacitors have higher internal resistance than aluminum electrolytic capacitors, so they cannot be used in AC circuits. (3) Battery cells are energy-intensive components with a longer discharge time, while supercapacitors are power-intensive components with a shorter discharge time, can't provide power for long time All supercapacitors contain a positive electrode, a negative electrode, and a membrane between the two electrodes, which acts as an insulator for electrons, a good conductor of ions and an electrolyte that fills in two pores separated by the two electrodes and the membrane. According to the different energy storage mechanism, supercapacitors can be divided into two types: double-layer capacitor and Faraday capacitor.

1.2 Principle of Capacitors

Capacitors, which store both charge and electrical energy, have been around since 1900 and are one of the most commonly used electronic components.

It is mainly composed of two metal plates and the dielectric with poor conductive performance between the two plates. When the power is applied to the two plates, the charge on the plate will move, and the potential difference will be formed between the two plates in a short period of time, when the potential difference is no longer changing. If the voltage between the plates can be applied to a certain electrical appliance, the electrical appliances will be seen to work for a very short time and then stop, which is the discharge of the capacitor. The capacitance and other parameters of the capacitor can be calculated by the following formula.

$$C=\frac{Q}{U} \tag{1}$$

C: capacitance
Q: charge
U: voltage

Equation (1) shows only the numerical relationship between the capacitance of the capacitor and the charge it carries and the voltage. In fact, the capacitor is determined by Equation (2) below.

$$C=\frac{\varepsilon s}{d} \tag{2}$$

C: capacitance
S: Plate area
D: Distance between plates
ε : The relative dielectric constant of the dielectric between the plates

In addition, Equations (3) and (4) express the calculation method of multiple capacitors in series and parallel circuits.

$$\frac{1}{C}=\frac{1}{C_1}+\frac{1}{C_2}+\frac{1}{C_3}+\cdots+\frac{1}{C_n} \tag{3}$$

$$C=C_1+C_2+C_3+\cdots+C_n \tag{4}$$

The main function of the capacitor is to block the direct current of the circuit through the alternating current mode. At the same time, it can store a small amount of charge and release it when the current is interrupted. It is a good current filter element.

Its main applications are in AC circuits, which output pulsating electrical signals in a smooth manner. For example, in the high-power AC circuit, there will be some inductive load containing the motor. This kind of electrical appliances will produce inductive electromotive force in the change of current, which will hinder the change of current. At this time, the speed of current increase or decrease will be slowed down, and no mutation can occur. At this time, the electromotive force in the circuit is always changing, which will lead to the situation that the current will lag behind the voltage by one phase. The application of capacitors in the circuit, the use of its in a short time can be fast charging and discharging characteristics plus some special circuit collocation can ensure the smooth output of the current in the circuit, can filter to correct the power factor in the circuit. This kind of capacitor is a static charge storage medium, which can keep its internal potential difference permanently. It is widely used in the part of electronics and power. It is mainly used in power filtering, signal filtering, filtering, compensation, charge and discharge, energy storage, DC isolation and other circuits.

1.3 Capacitor and batteries

Supercapacitors and batteries work in the part of same way: they can be charged and discharged when necessary. However, the battery exists as a power source in the circuit, while the capacitor is a component that behaves as a circuit breaker in the circuit. In the process of battery storage of electric energy, there will be a mutual conversion between electric energy and chemical energy, while the capacitor only stores charge to form potential, and when the external potential is lower than the capacitor, it will discharge. However, with the development of science and technology, the use of batteries and capacitors began to be similar. In the past, batteries usually provided a higher energy density in the circuit, while capacitors were used in the circuit for filtering waves and coupling because of their higher charge and discharge capacity. With the emergence of the demand for fast portable power supply, people began to study to increase the charging and discharging time of batteries, while increasing the storage capacity of capacitors, in order to seek longer life of batteries and capacitors with high energy to measure density. In the research process, the battery charging efficiency is low, resulting in environmental pollution shortcomings gradually do not meet the modern people's environmental protection concept; Capacitive supercapacitors are characterized by high charge-discharge times, long service life, wide temperature range, high cycle efficiency and environmental protection. It also suggests that slowing the rate at which capacitors discharge might lead to cleaner, more efficient storage devices. The emergence of supercapacitors also marks the use of clean energy to reach a new height.

1.4 Supercapacitors and batteries

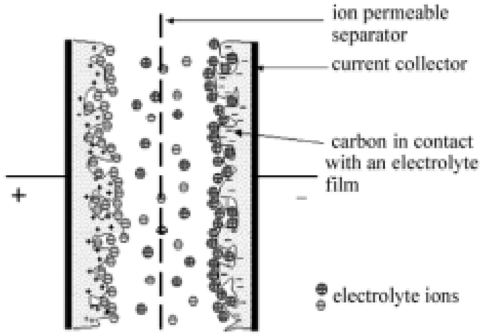
In the principle of battery production, people can know: inserted in the electrolyte solution of the metal electrode surface and both sides of the liquid will appear the sign of the opposite excess charge, so that the potential difference between the phase. In such a case, insert the two electrodes in the electrolyte at the same time, and apply a voltage between the two electrodes, if the voltage is lower than the voltage of the electrolyte decomposition, positive and negative ions under the action of electric field in the electrolyte moving quickly to the poles, and on the surface of two electrodes form close layer charge respectively, the charge is the electric double layer The electric double layer formed by this method is similar to the polarization charge generated by the dielectric in a conventional capacitor under the action of an electric field, resulting in a capacitance effect. The tight double layer is similar to that of a flat capacitor. In addition, since the close charge layer spacing is much smaller than the distance between charge layers of ordinary capacitors, we can know from Equation (2) that such capacitors have a larger capacity than ordinary capacitors. This kind of capacitor has a large internal resistance and can be charged without load resistance, so it has the characteristics of battery[4].

Because of the capacitor configuration, in the event of overvoltage charging, the capacitor will behave as an open circuit to avoid the loss to the device and can be charged without limit current. However, the technology of supercapacitors is not perfect and cannot completely replace the function of batteries. Therefore, in the fields of new energy vehicles and hybrid electric vehicles, the form of combination of batteries and supercapacitors is adopted to maintain the running of electric vehicles by taking advantage of the characteristics that batteries can provide stable current and taking advantage of the characteristics that capacitors have the advantages of large output power, rapid charge and discharge, and high recovery efficiency of braking regenerative energy. Supercapacitors can be used to store regenerative energy generated during braking, and provide energy during acceleration and climbing; at the same time, the battery can ensure the car can run smoothly for a long time. In this way, electric vehicles have the advantages of long driving time fast start, fast acceleration, strong climbing ability and so on. [5]

1.5 Type of supercapacitors

There are two types of supercapacitors, which are double-layer and Faraday quasi-capacitors

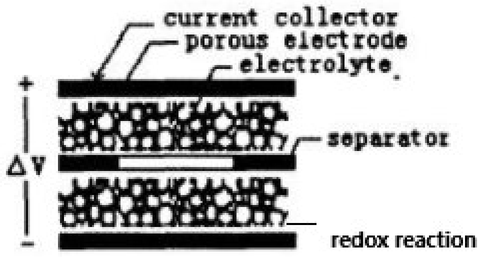
1.5.1 Electric double layer capacitor (EDLC)



(Figure 1: Operating principle of double layer capacitor) [6]

Such capacitors are generated by the charge confrontation at the electrode-solution interface caused by the directional arrangement of electrons or ions. [6] For an electrode-solution system, a double electric layer is formed at the interface between the electrically conducting electrode and the ion-conducting electrolyte solution. That is, when the electric field is applied on the two electrodes, The negative and cation in the solution move to the positive and negative electrodes respectively, and the electrons on the electrode plate will also move and attract each other with the ions in the solution, finally forming a double electric layer on the surface of the electrode. After withdrawing the electric field, the positive and negative charges on the electrode attract the opposite charge ions in the solution and make the double electric layer stable, resulting in a relatively stable potential difference between the positive and negative poles. At this time, for an electrode, the opposite ion charge equal to the charge on the electrode will be generated within a certain distance, so that it remains neutral. When the electrode is connected with the external circuit, the charge on the electrode will migrate and generate current in the external circuit, and the ions in the solution will migrate to the solution and become electrically neutral, which is the charge and discharge principle of the double-layer capacitor.

1.5.2 Faraday quasi-capacitance



（Figure 2: Faraday Quasicapacitor working principle, source: network, modified）

Such capacitors are electroactive substances deposited in two dimensional or quasi-two-dimensional space in the volume phases or on the surface and near surface of the electrode, resulting in highly reversible chemical adsorption-desorption and redox reactions, resulting in capacitors related to the electrode charging potential. For Faraday quasi capacitor, the charge storage process includes not only the storage on the double electric layer, but also the redox reaction between electrolyte ions and the electrode active material. [7] When the ions in the electrolyte (such as H+, OH-, K+ or Li+) are diffused from the solution to the electrode-solution interface under the action of an applied electric field, they will enter into the bulk phase of the active oxide on the electrode surface through the redox reaction at the interface, thus making a large amount of charge stored in the electrode. When discharging, these ions entering the oxide will be returned to the electrolyte through the reverse reaction of the above redox reaction, and the stored charge will be released through the external circuit, which is the charge-discharge mechanism of Faraday quasi-capacitor.

1.6 Application and development of supercapacitors

Miniaturized supercapacitors are already used in small mechanical devices, such as computer memory systems, cameras, audio equipment and auxiliary devices that use electricity intermittently. Large cylindrical supercapacitors are mostly used in automotive and natural energy harvesting. In terms of development over the next decade, supercapacitors will be an important part of the transportation industry and natural energy harvesting. For example, in the field of rail transit, in this paper we know that the super capacitor for storing new energy automobile braking energy, and supercapacitor larger output power can be used for vehicle speed, and the large number of subway station, it also led to the subway the need for frequent braking, acceleration, this with the working characteristics of super capacitor very conform to, The application of supercapacitor can not only reduce the speed increase time of subway, but also has great significance to the energy saving of subway. [8] In the field of power system, wind power generation and solar power generation are unstable, which requires frequent charging and discharging of energy storage equipment. The life of battery is short and the charging and discharging times are few, while the supercapacitor has a considerable number of charging and discharging times, which can greatly improve the reliability of the system and improve the power quality.

1.7 Supercapacitors and batteries

There are many factors that affect the performance of supercapacitors, such as the capacitance of the electrode material, the purity of the electrolyte, the test temperature, and the performance of the membrane between the electrolytes. [9] Among them, the purity of electrolyte and test temperature can be controlled variables, while the diaphragm only needs to isolate electrons and do not hinder the transport of ions. Therefore, we focus on the influence of electrode materials of supercapacitor on the performance and structure of supercapacitor. The supercapacitor stores energy in the charge separated. Therefore, the larger the area used for charge storage and the denser the charge separated, the greater the capacitance of the supercapacitor will be. In general, the area of a capacitor used to store charge is related to the area of the plate. To get more capacitance, people usually have to roll a very long material into a coil, and there is an insulating material between the two plates of a conventional capacitor, which greatly increases the size of the capacitor. With the continuous development of new materials, porous materials are gradually entering the field of capacitors, and some other measures can be taken to achieve a larger surface area in a smaller volume, that is, the emergence of porous materials gives supercapacitors a larger specific surface area. Moreover, the distance between supercapacitor charges is determined by the size of the electrolyte ions attracted to the charged electrode, which is relatively small compared to the thickness of traditional capacitor film materials. As a result, supercapacitors of the same size have more electrostatic capacity than ordinary capacitors. The materials of supercapacitors can be roughly divided into carbon materials, metal oxide materials and conductive polymer materials. [10]

1.7.1 Carbon materials

At present, activated carbon materials are mainly used as electrode materials for supercapacitors. Activated carbon materials have the basic characteristics of low cost and high specific surface area for making supercapacitors. But the microstructure of activated carbon material is in the form of micropores, so it is not easy to be soaked by electrolyte, and has a very large resistance, charging and discharging speed is slow. However, the easy availability of raw materials and the simplicity of manufacturing are also the reasons for the large market for active carbon materials. [11] Graphene has special thermal conductivity and optical properties, as well as high mechanical properties, and is a very hot research direction in the world. In 2004, two scientists at the University of Manchester in the United Kingdom, Andre Geim and Konstantin Novoselov, produced graphene using tape stripping. The special structure and elemental properties of graphene enable it to have good electrical conductivity: at any temperature between 50 and 500K, the room-temperature high carrier mobility of graphene is around 1000cm2/ (V·s). [12] Therefore, graphene is an ideal electrode material. However, the preparation of graphene is relatively difficult, and the simplest REDOX method cannot reduce graphene well. In addition, most of the reducing agents of graphene are highly toxic and not conducive to production. Therefore, graphene research is still a work in progress. In addition to the above representative carbon materials, there are only conductive aerogels -- carbon aerogels, carbon nanotubes with large specific surface area, relatively environmentally friendly activated carbon fiber and other electrode materials that can be used in supercapacitors are also in the stage of exploration and research.

1.7.2 Metal oxide material

Metal oxide is also a major types of super capacitor materials, its storage principle is different from the way of electric double layer of carbon material storage, it mainly using Faraday principle of capacitance, within the electrode plate and electrolyte interface can be rapid and reversible REDOX reaction, which makes this kind of capacitor of capacitance is far bigger than double-layer capacitance. Metal oxide electrode materials are divided into unit metal oxides, binary metal oxides and ternary metal oxides, and their conductivity also increases with the kinds of metals contained. Metal oxide materials have been widely introduced into the market due to their high energy density, large specific capacitance and low price, but they still have room for improvement due to the defects of low electrical conductivity. [13]

1.7.3 Conductive polymer material

Conducting polymer materials are mainly used in Faraday quasi-capacitors. Because of the strong plasticity of conducting polymer, it is easier to prepare thin electrode materials with low internal resistance. Conductive polymers as capacitor plate, when the capacitor charging and discharging will produce larger electric double layer on the surface of polymer material, at the same time conducting polymers will be carried out in REDOX reaction, quickly generate n or p type doping, which produce very big Faraday polymer for a very high density of charge capacitor, has the very high electrochemical activity. [14]

Chapter 2 Experiment

2.1 Introduction

This experiment mainly explores the electrochemical characteristics of polyaniline and nano-sized γ-Fe2O3 composite electrode materials.

Polyaniline is a conductive polymer with low cost and simple synthesis process compared with other materials, and it has excellent performance and wide application range among the conductive polymers. [12] The conductive mechanism of polyaniline is restricted by many factors, including the relative molecular weight of polyaniline, polymerization conditions, doping degree, and even the crystal structure of polyaniline. [15] Polyaniline in doping, due to protic acid decomposition of H+ and pair of anions (such as Cl-, SO42-, etc.) into the main chain, combine with and amine and imine group N atoms to form the pole and bipolar delocalization to the whole molecular chain π bond, so that polyaniline presents a high conductivity. In the process of preparing polyaniline particles, transition metal oxide nanoparticles can be added to prepare polyaniline doped with transition metal oxide. The electrochemical performance of polyaniline is greatly improved by the doping of transition metal ions. The specific capacitance and impedance of polyaniline doped with transition metal ions are higher than that of undoped polyaniline. [16]

2.2 Experimental Section

2.2.1 Experimental raw materials

name	specification	source
aniline	ACS,⩾99.0%	Shanghai Aladdin Biochemical Technology Co., Ltd
γ -Fe2O4	10nm,98% metals basis, γ type	Shanghai Aladdin Biochemical Technology Co., Ltd

2.2.2 Experimental Instruments

Instrument	type	place of production
Electrochemical interface analyzer	iviumstat.h	Ivium Technologies BV
Ultraviolet and visible spectrophotometer	UV28OOS	Shanghai Sunny Hengping Scientific Instrument Co., Ltd
Fourier transform infrared spectrometer	Nicolet IS50	Thermo Fisher Sclentific

2.2.3 The experimental method

Electrochemical method

Electrochemical polymerization is in electrolyte solution containing a certain concentration of aniline, using appropriate base (such as platinum foil) as anode, select the appropriate electrochemical conditions, that is control anode voltage and anode current density, use control-potential method or Potentdynamic scanning method, a dense film with points attached to the electrode surface was produced on the anode. This experiment is using cyclic voltammetry (Potentdynamic scanning method). [17]

2.2.3 Preparation of polyaniline and its composites

(1) Weighed 0.1596g γ-Fe_2O_3 and diluted it with water to 50ml

(2) The aniline was divided into three groups, each group contained 227 μl aniline. The first group was diluted to 50 mL with 1mol/L sulfuric acid.

(3) The second group was diluted to 50ml with 0.1mol/L sulfuric acid, and the third group was diluted to 50ml with 0.01mol/L concentrated sulfuric acid.

(4) ITO glass was cut into cuboids 5cm in long and 0.6cm in width, and then cleaned with acetone and distilled water to remove residual organic impurities on the glass surface.

(5) Electrochemical preparation of polyaniline. The amount in the first set of aniline solution takes 5 ml solution, on glassy carbon electrode as working electrode, carbon rod as the counter electrode, Ag/AgCl as reference electrode, immerse the electrodes in aniline solution, The electrochemical interface analyzer performs cyclic voltammetry electrochemical synthesis, and the final polymer will be formed at the working electrode and near the area. Among them, the voltage range is 0-1V, the scanning rate is 50mV/s, the E step is 2mV, and the number of scanning turns is 20. The second group and the third group were combined in the above steps. After that, another 5ml solution was taken from the three groups of aniline solutions, and the glassy carbon electrode was replaced with ITO glass electrode. Take the same data and repeat the above steps for synthesizing.

Electrochemical preparation of aniline and γ-Fe_2O_3 composites. Three groups of aniline reagents were mixed with γ-Fe_2O_3 in the ratio of 1:1, 2:1, 4:1, 8:1, 16:1, 32:1 to form 5mL of mixed reagents, and each electrode was immersed in the mixed reagent. Glassy carbon electrode and ITO glass electrode were still used as working electrode and repeat the above steps for electrochemical synthesis.

(6) Product Performance Analysis. The electrode with polymer was immersed in 5mL, 0.1mol/L potassium chloride solution, the reference electrode and counter electrode remained unchanged, and the other parameter remained unchanged. Use cyclic voltammetry scan the product by the scanning rates were 10 mV/s, 20 mV/s, 50 mV/s, 100 mV/s, and 200 mV/s respectively. Then use the cyclic voltammetry to analyze the properties of the product.

Through the image we can know in which pH, proportion, electrode the synthesis of aniline-γ-Fe_2O_3 composite material have the best performance. Then use Fourier transform infrared spectrometer and UV-Vis spectrophotometer to explore the structure and properties of the product.

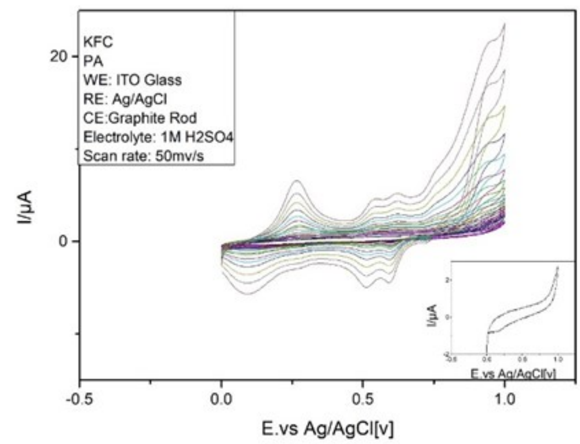
Chapter III Conclusions

3.1 The data analysis

By comparison, it can be concluded that the composite product is better when 1mol/L sulfuric acid is used as the buffer solution, ITO glass is used as the working electrode, and PA: γ-Fe_2O_3=4:1.

Due to the large number of measured data in the experiment, this paper will not show all the images, only show the cyclic voltammetry curve of polyaniline (as a control) and the cyclic voltammetry curve of PA: γ-Fe_2O_3=4:1 (the experiment shows that this ratio of products with the best product ratio) for comparison, to find out the advantages of the product over polyaniline.

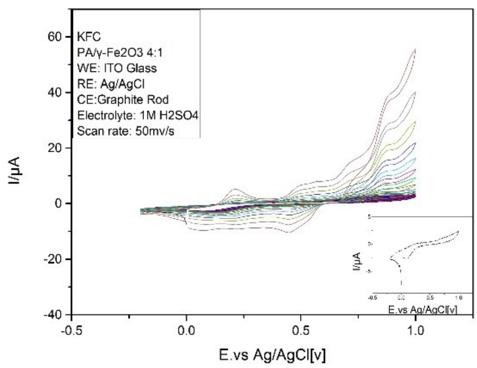
3.1.1 Electrochemical synthesis curve

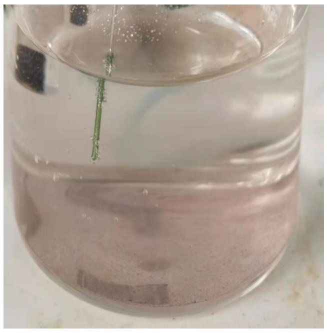


(Figure 3: Graph of electrochemical synthesis of polyaniline)

In this set of figures, it can be seen that polyaniline has three pairs of reversible redox peaks. From the top left, the first peak marks the synthesis of fully reduced polyaniline, the middle peak is the synthesis of intermediate oxidized state polyaniline, and the third peak is the synthesis of fully oxidized state polyaniline.[18]

The three relative peaks below represent the three reduction peaks respectively. Perhaps due to some problems in the experimental treatment, the peak of the intermediate oxidation state is not particularly obvious.



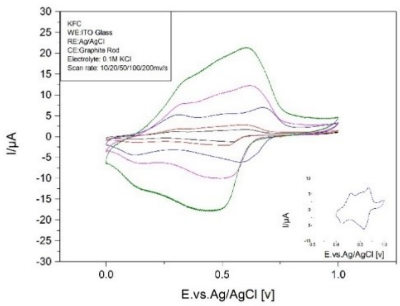


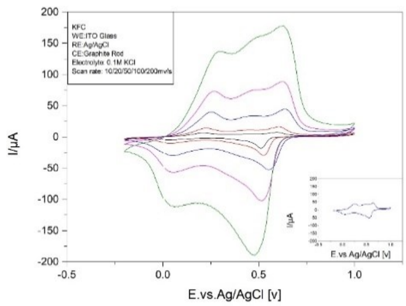
(Figure 4: Electrochemical synthesis of polyaniline with γ-Fe_2O_3.)

(Photo 5: Products shed during electrochemical synthesis)

The curve in Fig. 4 is particularly compact, with no obvious intermediate oxidation state formation. It is speculated that the ITO glass is too smooth, resulting in the shedding of some products during the REDOX reaction, resulting in the curve cannot well reflect the efficiency of synthesis. Figure 5 shows the organic composite material shed during synthesis. The green flocculent floating material in solution is the synthetic product.

3.1.1 Analytical curve

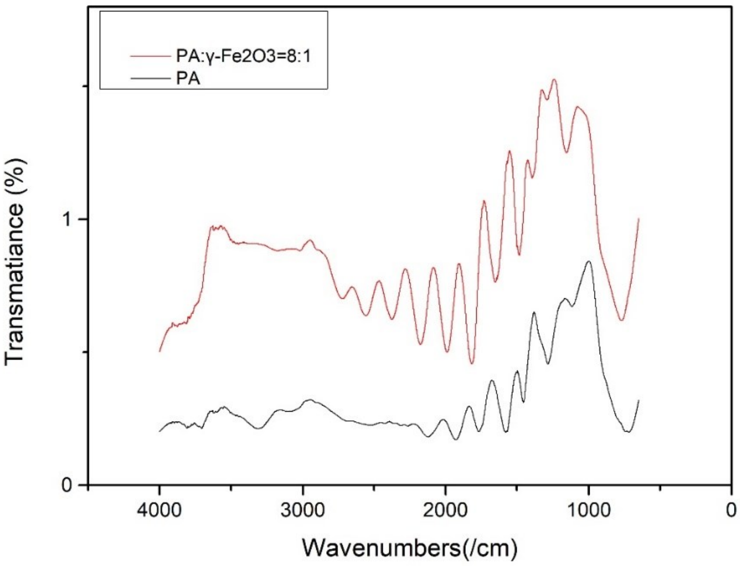




(Figure 6: Conductivity test of polyaniline.)

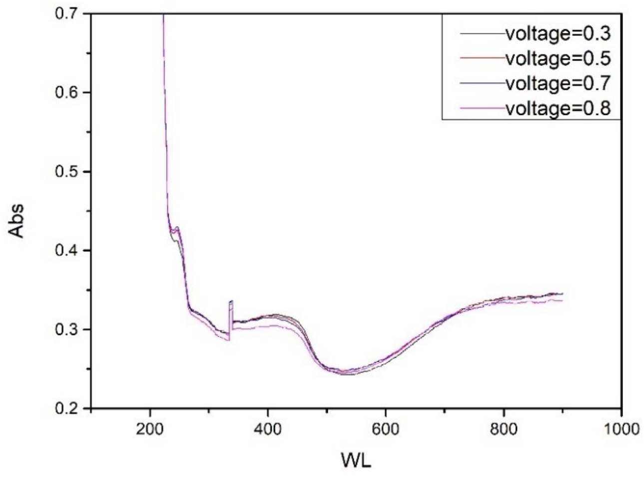
(Figure 7: Polyaniline: γ-Fe_2O_3= 4:1 product test of electrical conductivity)

Through the comparison between Figure 6 and Figure 7, we can clearly observe that the composite material has better electrical conductivity. In the test chart, the characteristic peak of the intermediate oxidation state of Polyaniline: γ-Fe_2O_3= 4:1 product is more obvious (Contrast that with a composite curve). It can be known that: polyaniline and γ-Fe_2O_3 formed composite material than polyaniline polymer in the performance of a multiple of improvement.



（Figure 8：Polyaniline and conform to the infrared curve of the product）

In infrared figure 8, we can clearly observe the characteristic curve caused by the stretching vibration of covalent bond. The black curve is aniline, and the red curve is composite material. The stretching vibration of the carbon-carbon double bond in the benzene ring can be seen at 1400-1500cm^{-1}, the absorption peak of the weak carbon-hydrogen single bond can also be seen near 3000cm-1, and the absorption characteristic peak of aromatic amine can be seen obviously near 1000^{-1}. [19] However, in 2000-2500cm^{-1}, there was a wavy curve. After comparing the absorption chart, it was speculated that this was caused by the organic impurities on the surface of ITO glass that were not cleaned.



（Figure 9: Ultraviolet absorption curve of composites）

The transition from π to π* can be observed obviously in the infrared image, and the characteristic peak of the amino group on the benzene ring can be observed near the value 200. [20] However, there is a big jump in the curve around 350-360, which is caused by the spectrophotometer switching the light source.

3.2 Summary

Through the screening of the ratio of aniline and γ-Fe_2O_3, the most effective ratio for the synthesis of target materials was roughly obtained through the transverse comparison. Through longitudinal comparison, it is found that the target material can effectively improve the performance of the electrode material, which has a positive significance for the development of supercapacitors and the utilization of new energy.

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