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Preparation and Properties of Graphene-Based Flexible Electrodes Based on Thermal Convection

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Abstract: Graphene is one of the most interesting matrix materials for constructing flexible supercapacitor electrodes due to its high electrical conductivity, high specific surface area, excellent mechanical properties, and ease of assembly. In this paper, the preparation and properties of graphene-based(GB) flexible electrodes based on heat transfer and convection are mainly studied. This paper firstly introduces the preparation methods of graphene materials and the research progress of flexible electrodes, and discusses the current application environment of GB flexible electrodes. In this paper, graphene oxide (GO) hydrogel was used as raw material, and water-soluble manganese salts (anhydrous manganese sulfate and manganese acetate) were used as manganese source, and graphite oxide was prepared on flexible conductive substrate (titanium foil) by doctor blade coating method. The olefin-Mn2+ composite film is then used for laser sintering. The high temperature at the laser focus reduces GO to reduced graphene oxide (RGO) and simultaneously cracks the manganese salt into manganese dioxide at high temperature, thereby fabricating a flexible composite electrode.

1. Introduction

Due to the development of wearable electronic devices, flexible wearable electronic devices are an important development direction of current electronic devices. Although the flexible LED display technology has become more mature and has been applied in some communication devices, because its energy storage devices and other electronic devices are not flexible, the entire device cannot be made into a flexible device [1]. Lithium batteries are limited by the complex composition of their electrolytes, and solid electrolytes also have problems such as interface contact and poor ionic conductivity, so the preparation of flexible lithium-ion batteries is still relatively difficult. Supercapacitors have a wide range of electrolyte options, ranging from aqueous electrolytes to organic electrolytes, as well as quasi-solid gel electrolytes, which can well meet the performance requirements of supercapacitors. Due to the special two-dimensional nanosheet structure and van der Waals forces between sheets, graphene can be designed and assembled into macroscopic graphene films, but as a flexible electrode material, it often exhibits mediocre capacitive performance. Because the theoretical electric double layer capacity of a single-layer graphene sheet is ~21 μF cm-2, when the surface of the nanosheets on which the graphene film is constructed fully adsorbs electrolyte ions, its specific capacity can reach 550 F g-1. However, due to the The agglomeration of nanosheets leads to the reduction of the effective specific surface area of the membrane electrode, and the obtained capacitance value is often much lower than the theoretical value [2-3]. To this end, some scientific researchers improve the microstructure of graphene films by adjusting the preparation process, so as to alleviate the problems of graphene sheet agglomeration, and achieve the purpose of optimizing the capacitance performance of graphene films [4].

Graphene has two-dimensional properties, and physical and chemical methods can be used as a basis to assemble flexible films or bulk materials [5]. In 2007, foreign scholars first applied vacuum filtration to prepare graphene oxide films, and studied their mechanical properties, which provided the possibility for the preparation of flexible GB films [6]. Domestic scholars have prepared a highly conductive flexible graphene film by vacuum filtration. Qijing is similar to graphene oxide film, and also has high conductivity, indicating that graphene film is used in the field of flexible supercapacitors. The application has potential application prospects [7]. Since then, GB flexible films have received more and more attention in the field of flexible supercapacitor electrode materials. Thin film materials with diverse structures prepared from graphene are widely used as electrode materials for supercapacitors [8]. Although many literatures have studied the regulation of the structure of graphene films for flexible supercapacitor electrodes and the introduction of the second phase, and good results have been obtained [9]. However, there are few systematic studies on the structure and composition regulation of flexible GB electrode materials, especially the preparation of GB flexible electrodes prepared by thermal convection based on heat transfer.

At present, some progress has been made in the development of flexible GB supercapacitors. The methods that are often used to improve the performance of supercapacitors include: reducing the thickness of the electrode material to obtain high gravimetric capacitance; increasing the specific surface of the electrode for Charge storage provides more active sites; optimizes the pore structure of the material to facilitate the diffusion of ions. Moreover, the optimization of electrolytes, current collectors, and supercapacitors as a whole is also critical. Although methods have been developed to improve the flexibility of supercapacitors by reducing their thickness, the device is prone to short circuits, and thus, developing highly safe flexible supercapacitors remains a challenge.

2. Graphene Materials and Applications

2.1. Introduction to Graphene Materials

(1) Graphene preparation method

There are many ways to synthesize graphene, but in general, it can be divided into two categories. The first is to exfoliate graphene sheets from graphite; the second is to synthesize graphene from other carbon sources. Among the many synthesis methods, mechanical exfoliation and chemical vapor deposition (CVD) are the most suitable for producing single-layer graphene, but these two methods have low yields and are difficult to achieve large-scale industrialization [10]. The most important synthesis method in the actual production process is the graphene oxide reduction method, the principle of which is shown in Figure 1.

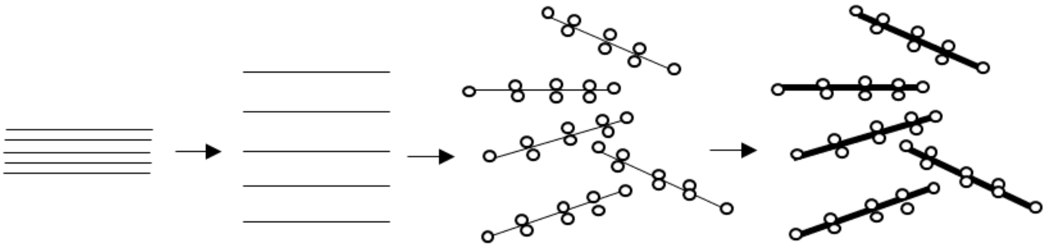

Figure 1. Schematic diagram of graphene preparation by redox method

(2) Electric double layer capacitance of graphene materials

The properties of carbon materials suitable for electric double layer capacitors include large specific surface area, good electrical conductivity, good chemical stability, and good contact between the surface and the electrolyte. Graphene is undoubtedly an electrode material that meets the above conditions, but similar to many traditional carbon materials, some of its own characteristics still affect the electric double layer capacitance [11].

The conductivity along the plane of the hexagonal crystal system and the conductivity in the vertical direction are very different in graphite crystals, which is similar in graphene [12]. The transport efficiency of electrons in a single graphene sheet is much higher than the transport efficiency of electrons between graphene sheets in contact with each other, which means that the size of graphene sheets suitable for electric double layer electrode materials needs to be as large as possible , to reduce the probability of electron transport between graphene sheets [13]. At the same time, the formation of van der Waals forces and π-π bonds between graphene sheets makes its actual specific surface area much lower than the theoretical value. To obtain a larger specific surface area, it is necessary to control the stacking of graphene sheets. Therefore, graphene nanosheets The control of layer size and film formation uniformity is crucial for the formation of graphene films with high specific surface area and low conductivity.

The interlayer spacing of graphene sheets in the electrode material and the pore structure of the graphene layer will also affect the electric double layer capacitance, and the distribution of different interlayer spacing and pore structure will affect the diffusion of electrolyte ions on the surface of the material [14]. For different interlayer distances, the diffusion barrier of charged ions between layers is different, and a larger stacking distance of graphene sheets will make the diffusion of ions easier; and the pore structure and distribution will not only affect the specific surface area of the material, when When the ions can pass through the macroporous structure, the diffusion distance of the ions in the material will be shortened, but when the pores are too small, the ions cannot enter, which will reduce the effective specific surface area of the material [15].

The functional groups on the carbon surface in the electrode material also have an effect on the capacitance. In fact, the carbon surface in graphene still has some oxygen-containing functional groups, which generally exist at the edge of the graphene sheet, and the number is approximately proportional to the specific surface area of the material. That is to say, graphene still has a certain redox activity, and the corresponding pseudocapacitance Cφ will be generated with the main electric double layer capacitance CDL, and is almost proportional to the value of CDL [16].

(3) GB flexible electrodes

Soon after the concept of transparent flexible supercapacitors, graphene became the focus of research in this field due to its excellent mechanical and optical properties. Some scholars have used hydrazine vapor to reduce the GO thin film prepared by spin coating. The square resistance of the prepared thin film electrode is 100-500 Ω sq-1, and the light transmittance at the wavelength of 550 nm is about 80%. These studies have proved the possibility of graphene as a transparent flexible electrode, but the specific capacitance obtained is relatively low due to the low actual specific surface area of graphene and the large equivalent series resistance of the electrode in the above studies.

The rules for developing high-performance GB flexible electrodes can be summarized as follows: On the basis of ensuring good flexibility and high cycle life, the specific capacitance performance of the electrode can be improved by improving the electrode conductivity or optimizing the graphene structure.

2.2. Applications of GB Flexible Electrodes

(1) Super capacitor

A supercapacitor, an energy storage device, can be safely charged or discharged, usually within seconds, with an extremely long cycle life. With excellent mechanical strength, high specific surface area, and good electrical and thermal conductivity, graphene has become one of the most promising candidates for supercapacitor applications [17]. In recent years, a variety of graphene materials, including graphene fibers, graphene films, and three-dimensional porous graphene frameworks, have been synthesized to enhance the performance of supercapacitors.

Pure graphene fibers usually have only small capacitance due to their low specific surface area and poor hydrophilicity. In addition to good electrochemical performance, scaling up of capacitive performance is crucial if these flexible supercapacitors are to be realized for practical applications.

(2) Sensor

Conventional sensors are rigid, so there are rigid barriers to capturing analytes, as well as poor conversion capabilities. Flexible sensors can capture analytes more sensitively, detect targets with high selectivity, and can generate excellent electrochemical signals. GB materials are widely used in flexible sensors due to the excellent stability and mechanical flexibility of their lattice structures. Flexible sensors can be divided into pressure sensors, temperature sensors, humidity sensors, etc. according to their different functions. Due to the abundant presence of oxygen-containing functional groups in rGO and its large molecular adsorption specific surface area, GB flexible humidity sensors have become a research hotspot due to their potential applications in biomedicine and electronic skin [18].

GB flexible humidity sensors have high sensitivity, excellent flexibility, good ductility and stability, and have great application potential in electronic skin, personal health monitoring, wearable and stretchable humidity sensors and other fields. They can be placed on the human body or clothing, detect signals of human activity, and obtain various physiological information depending on the realized object.

3. Preparation of GB Flexible Electrodes

3.1. Laboratory Instruments and Medicines

The instruments and medicines used in the preparation of GB flexible electrodes in this paper are shown in Table 1 and Table 2.

Table 1. Experimental instrument and model

Instrument name	Manufacturer
Magnetic stirrer	Shanghai sile Instrument Co., Ltd
Drying box	Shanghai Yukang science and Education Equipment Co., Ltd
Electrochemical workstation	Shanghai Chenhua Instrument Co., Ltd
Gas meter	Shanghai silver automation
Ultrasonic cleaner	Kunshan Ultrasonic Instrument Co., Ltd
Electronic balance	Mettler Toledo (Shanghai) Co., Ltd
Field emission scanning electron microscope	Hitachi, Japan
X-ray photoelectron spectrometer	China

Table 2. Experimental drugs

Reagent name	Specifications
Manganese sulfate	Analytical purity
Manganese acetate	Analytical purity
Anhydrous sodium sulfate	Analytical purity
Potassium chloride	Analytical purity
Concentrated nitric acid	Analytical purity
Ethanol	Analytical purity

3.2.Preparation of Electrode Materials

Cut the flexible conductive base titanium foil into a rectangle with a length of 16 cm and a width of 9 cm, put it into a large beaker, first add 5% detergent, ultrasonically clean it for half an hour at room temperature, and then ultrasonicate the same length with deionized water. time, and finally use absolute ethanol followed by ultrasound for half an hour, take it out and put it in another large beaker containing absolute ethanol for later use. Graphene oxide hydrogel with GO content of 8 mg/g was used as raw material, manganese source was added, and the mixture was electromagnetically stirred at room temperature overnight to prepare a uniform manganese salt/graphene oxide hydrogel mixture. The titanium foil was uniformly coated using an automatic coating machine, that is, the knife coating method, and dried at room temperature. Finally, a laser engraving machine is used for in-situ reduction to prepare a graphene-manganese oxide composite electrode material.

4. Properties of GB Flexible Electrodes

When the CTAB solution concentrations were 0.1 mg mL, 0.3 mg mL, and 0.5 mg mL, the prepared VRGO films were named VRGO[1], VRGO[2], and VRGO[3], respectively. As shown in Fig. 2, at a scan rate of 100 mV s-1, when the ordinate of the CV curve is the area current density, the integral area of the CV curve of the VRGO film decreases with the increase of the CTAB solution concentration. When the ordinate is the mass current density, the integral area of the CV curve does not change significantly, as shown in Figure 3. From these two results, it can be seen that the area specific capacitance of the VRGO film increases with the film thickness, while the mass specific capacitance value remains basically unchanged, which proves that the VRGO[1] with the largest load can also be fully infiltrated by the electrolyte. , and during the charging and discharging process, its active materials are maximized. However, due to the non-uniform reduction inside the VRGO film, its electron transport performance is poor, resulting in devices based on this material having a large internal resistance (Rs), and all CV curves show poor current response.

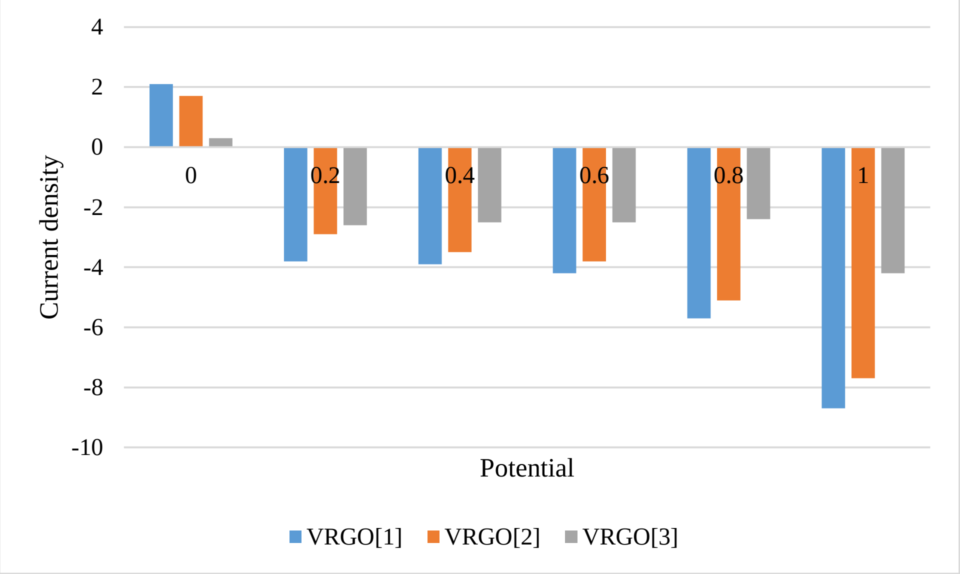

Figure 2. Area specific capacitance CV Curve

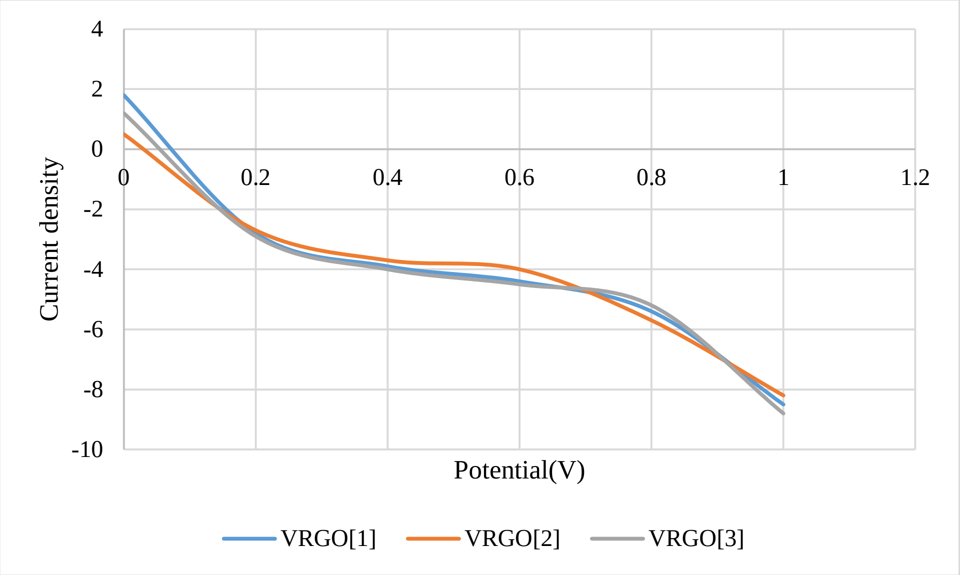

Figure 3. Mass specific capacitance CV Curve

5. Conclusion

GB materials have become potential supercapacitor electrode materials due to their large specific surface area, high electrical conductivity, light weight, and excellent mechanical properties. Although the preparation method of graphene and its electrochemical performance as a supercapacitor electrode material have been studied in this paper, there are still many key problems to be solved for commercial application. On the one hand, it is still challenging to prepare high-conductivity, high-quality defect-free graphene by a simple and low-cost method. On the other hand, high-performance flexible GB electrode materials require further development, which needs to ensure both high capacitance and excellent rate performance, as well as excellent cycling stability. A deeper understanding of the storage mechanism of supercapacitors is needed, especially for the interfacial reactions between electrodes and electrolytes, as well as the rational design of internal porous structured electrodes and layered interconnected porous electrode materials.

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Data Availability

Data sharing is not applicable to this article as no new data were created or analysed in this study.

Conflict of Interest

The author states that this article has no conflict of interest.

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