Preparation of transition metal oxide mixed graphene electrode materials and its application in supercapacitors

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Abstract:

The increasing prevalence of wearable electronic devices in contemporary society has led to heightened expectations for energy storage devices. These expectations encompass not only high power density and energy density, but also robust stability and resistance to bending. Consequently, the design and development of supercapacitors with versatile functionalities has emerged as a prominent area of research. The electrode material, which is one of the elements that can have the biggest impact on the operation of supercapacitors, has been the subject of numerous scientific advancements over the years. One promising approach is the combination of transition metal oxide and graphene material composite. By conducting a comprehensive review of relevant literature, this study synthesizes preparation methods from multiple sources, integrates the benefits of multiple technologies to develop a novel preparation method utilizing ultrasonic shock and the two-step interface self-assembly method, and compares the physical and chemical properties of different transition metal oxide mixed graphene electrode materials and their application in supercapacitors. In conclusion, the preparation methods of transition metal oxide mixed graphene electrode materials typically control their microscopic morphology in order to support structure, agglomeration, and spalling reduction, thereby enhancing the specific capacitance and cycle stability of supercapacitors and achieving the desired result of increasing specific surface area and support structure.

Keywords: graphene, transition metal oxide, supercapacitor, electrode material

1. Introduction

1.1 Research Background

The increasing advancement of electronic technology has led to a corresponding rise in the demand for flexible wearable electronic devices, including but not limited to electronic watches, flexible sensors, electronic skin, bendable screens. The use of supercapacitors has occurred[1]. When integrated with supercapacitors, it can function as an exceptional energy storage component in an extensive range of flexible wearable electronic devices. The utilization of graphene in electrode materials shows great promise due to its exceptional electrical conductivity, thermal conductivity, and mechanical properties. Moreover, the diverse methods employed in its preparation impart distinct physical and chemical characteristics to graphene, thereby augmenting its potential in the realm of battery electrodes. Graphene is susceptible to agglomeration stacking and other issues that significantly reduce its specific surface area below its theoretical value, thereby severely restricting its applications[2], despite its high specific capacitance and excellent electrical conductivity.(1) Heteroatom doping; (2) Composite formation of graphene and other substances.

The exploration of graphene's modification through the amalgamation of other substances to generate composite materials has been the subject of extensive research since its initial discovery (Figure 1-1a). Composite materials consisting of graphite and transition metal oxides exhibit exceptional performance in the domain of electrodes. Furthermore, there has been a steady influx of pertinent literature on this subject over the years (Figure 1-1b). Thus, it is evident that the formation of composite materials by combining transition metal oxides and graphene is a highly promising area of research. This is primarily due to the fact that transition metal oxide is a type of material[3] with a variety of different valence states and structures, its REDOX ability is very good, the ionic microstructure required as an electrode is very good, and its poor ionic conductivity and relatively simple electrode can be perfectly complementary with graphene materials.

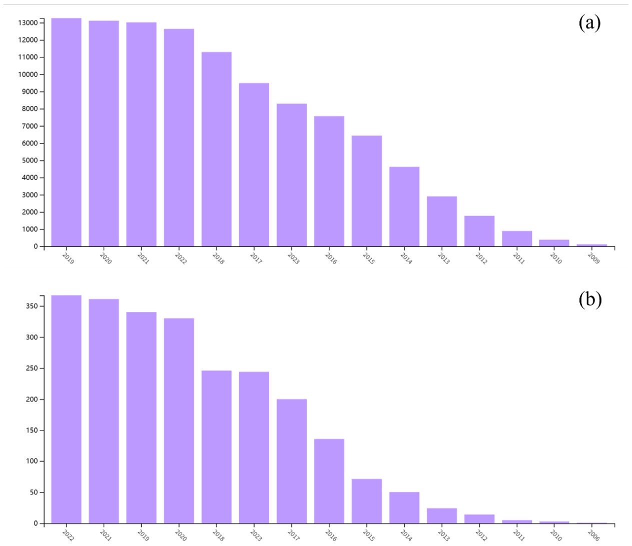

Figure 1-1 (a) The trend of the number of articles published on graphene composites; (b) Trend in the number of published articles on transition metal oxide mixed graphene electrode materials

This subject will provide a comprehensive overview of the attributes and benefits associated with diverse preparation techniques utilized in the fabrication of transition metal oxide mixed graphene electrode materials. It will also analyze and compare the physical and chemical properties of various graphene composites, as well as their performance in practical applications. Furthermore, it will draw conclusions and propose avenues for future research in the realm of graphene electrodes. In order to serve as a point of reference for the advancement and utilization of graphene in the domain of battery electrodes.

1.2 Introduction to supercapacitors

Four components comprise supercapacitors: diaphragm, electrolyte, electrode material, and fluid collector. Typically, the electrode material must be mixed prior to being uniformly coated onto the surface of the collector material. This is done to reduce the internal resistance of the collector material. To enhance current gathering capacity and facilitate current output, the thickness of the fluid collector and the slurry must be equivalent. The diaphragm serves two primary functions: to facilitate the purpose of ion entry and exit, to screen out a specific volume of charged particles in order to enhance the charge storage capacity, and to effectively separate the positive and negative electrodes to avert the risk of an internal short circuit that could result in harm. The capacitive performance of the device is significantly influenced by the electrolyte, which serves as a carrier of charge transfer. Water, organic, and ionic liquids are common electrolytes[1].

The three main categories of supercapacitors are asymmetric supercapacitors, pseudocapacitors, and electrical double-layer capacitors, with the storage mode of charge serving as the defining characteristic among them. In order to complete the storage, the former accumulates the pure electrostatic charge on the electrode surface, whereas the latter stores and discharges it[4]

(1)Electrical Double-Layer Capacitor (EDLC)

Helmholtz initially introduced the notion of EDLC in 1887, when he presented the Helmholtz double electron layer model. Figure 1-2 illustrates the EDLC principle. Upon the application of an electric field to the two electrodes, the ions and cations in the electrolyte will migrate to the positive and negative electrodes, respectively, and a double electron layer circuit will form on the electrode surface. The discharge of the artificially generated electric field on the electrode results in the dissipation of the charge that has accumulated on the electrode surface throughout the charging procedure. Therefore, a return to the solution is necessary to finalize the discharge procedure.

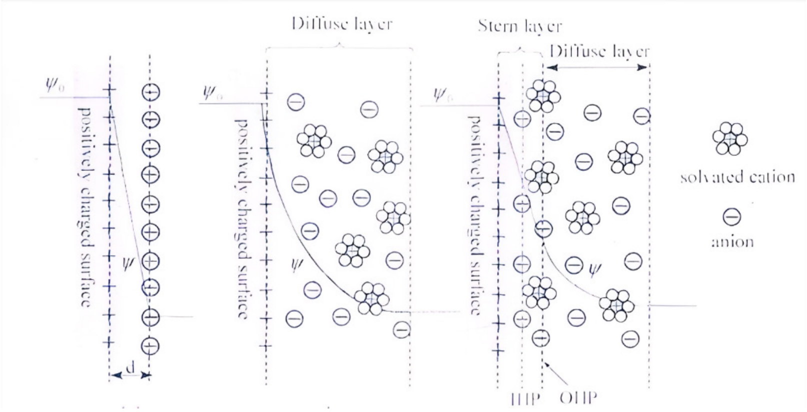

Figure 1-2 Energy storage mechanism of EDLC[5]

(2)Pseudocapacitors

The energy storage mechanism of pseudocapacitors differs from that of EDLC in that it involves a Faraday process and a highly reversible REDOX reaction occurring on the electrode. This Faraday process results in the deposition of an electric charge either on the electrode surface or in the two-dimensional or quasi-two-dimensional space within the body phase, ultimately forming the pseudocapacitor[6]

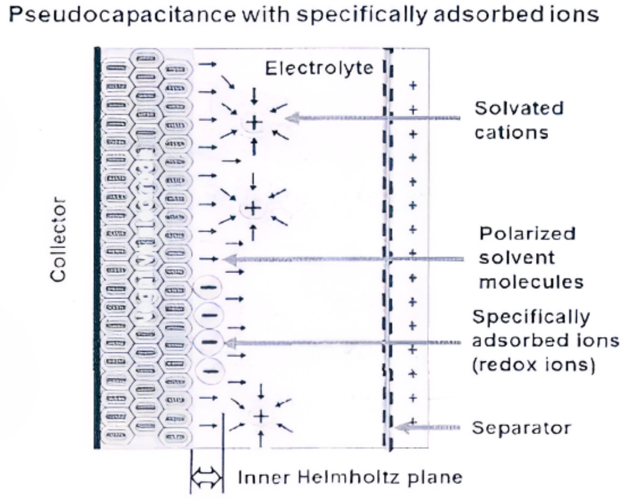

Figure 1-3 Storage mechanism of pseudocapacitor supercapacitors[5]

(3)Asymmetric supercapacitors

The utilization of distinct positive and negative electrodes in the asymmetric structure of the supercapacitor results in complementary expansion of its electrochemical window, which substantially enhances the voltage window[7] of the capacitor. The formula for calculating the energy density of supercapacitors is:

$$E=\frac{1}{2}CV^{2}$$

Since the energy density of supercapacitors is directly proportional to the square of the voltage window , it is more efficient to increase the voltage window rather than the capacitance in order to increase the energy density of asymmetric supercapacitors.

2. Preparation of graphene composite materials

Long-term research is devoted to the preparation method of transition metal oxide mixed graphene electrode materials, which has numerous practical applications, is based on a variety of theories, and each preparation method has its own set of advantages and disadvantages. Chemical vapor deposition (CVD), hydrothermal, microwave, ultrasonic dispersion, and two-step interface self-assembly are some of the methods that are considered to be approximate categories for the preparation of transition metal oxide mixed graphene electrode materials. The subsequent sections of this paper will provide an introduction to the preparation methods utilized in the aforementioned essential transition metal oxide mixed graphene electrode materials.

2.1 Chemical Vapor Deposition (CVD)

Two-dimensional material preparation frequently involves chemical vapor deposition (CVD). By utilizing gaseous carbon sources to deposit and react on the surface of transition metal oxides in order to produce graphene films, CVD operates on this principle. Although this approach has the capability to produce graphene films with a substantial surface area and high quality, it also presents challenges in terms of transferability to alternative substrates. The transfer method is notably intricate, resulting in a low deposition efficiency and the deposition of flammable gas that readily gives rise to safety concerns. Liu[8] et al. employed acetylene as a carbon source, and anneal the HF etched TiO_2 substrate for three hours in an air environment before increasing the temperature to 650°C in an argon environment and introducing acetylene and hydrogen to maintain a certain growth time. By manipulating the concentration, temperature, and growth time of the gas mixture, this technique is capable of altering the product's thickness.

2.2 Hydrothermal method

In recent years, hydrothermal methods have gained popularity as a means of preparing graphene. These methods offer the benefits of mild reaction conditions and high yield. Fundamentally, precursor solution of the target material undergoes a hydrothermal reaction with the graphene suspension at a specific temperature; the resulting composite solution is then calcined at a high temperature to produce the final composite material

Numerous developments in hydrothermal methods have transpired as a result of the innovation of scientific researchers over an extended period of time, surpassing the capabilities of the conventional approach in every respect.

Rafiq[9] et al. devised a procedure for the fabrication of NiO/rGO composites. NiO was produced via hydrothermal means at a temperature of 60℃. The novelty of this approach resides in the utilization of a low temperature wet chemical method to produce NiO, thereby reestablishing the temperature threshold of the hydrothermal method. The resulting NiO/rGO composite exhibits a specific capacitance of 883C/g and retains a high capacitance of 92.7% even after 3500 cycles.

Ling[10] et al introduced a straightforward method for fabricating hollow V_2O_3/carbon nanosphere electrode materials via low-temperature glucose-assisted hydrothermal annealing. To produce VO2O3 precursor, the glucose solution was added to acetyl acetone vanadium, which was then heated to 170 °C in an autoclave for 24h. Following this, the precursor powder was dried and the temperature was increased to 500 °C in a tube furnace. Lastly, the V_2O_3/ carbon nanospheres were kept in an air atmosphere for 1.5h. The V_2O_3/carbon nanospheres prepared by this method maintain a hollow spherical structure with a diameter of about 750nm. They also possess a substantial electrochemical reactive area and high porosity. Furthermore, even after 10,000 cycles, the specific capacitance remains unchanged at 98.39%, indicating commendable electrochemical stability.

2.3 Solid-state microwave method

Microwave method has gained prominence as a rapid and practical technique for fabricating graphene composite materials in recent times. The fundamental idea is that graphene, as a material with strong wave-absorbing ability, absorbs the energy supplied by the microwave and transfers it to the metal salt attached to it, promoting its oxidation and decomposition into metal oxides to produce mixed metal oxide electrode materials. In order to avoid the heat flow reverse phenomenon that occurs in conventional heat transfer, this method uses electromagnetic transmission as its energy source. As a result, the material is uniformly heated, which speeds up the nucleation growth of particles [11].

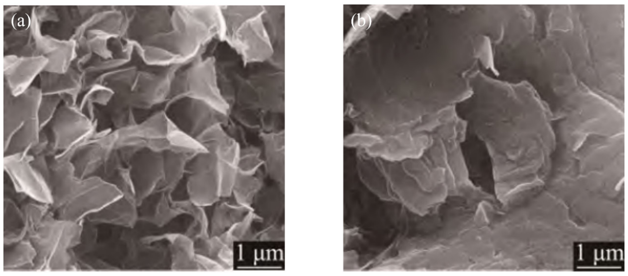

Figure 2-1 (a) SEM diagram of graphene; (b) SEM images of ZnO/G composites[12]

Hu[12] et al introduced a technique for fabricating ZnO/G composites. Not only is this method economical, quick, and convenient, but it also enhances the electrocatalytic capability of ZnO/G composites produced by the method (Figure 2-1) and reduces the folding defects of graphene, although this improvement is not readily apparent.

2.4 Ultrasonic dispersion method

The objective of the ultrasonic dispersion method is to create a uniform composite material from graphene and transition metal oxide particles in the precursor solution by utilizing the mechanical action of ultrasound. This method's operation is extremely streamlined, and the resulting product possesses a consistent shape, uniform distribution, and high purity; however, industrial production is challenging and equipment requirements are stringent.

Chen[13] et al. utilized a solution containing rGO and ZrO_2, mixed the two in a specific proportion, and then added a trace amount of chitosan. Solutions of rGO and ZrO_2 could be obtained following a 30-minute ultrasonic dispersion. It was then possible to obtain the rGO/ZrO_2 electrode by applying it to the treated glass carbon electrode and allowing it to dry naturally. This method yields a rGO/ZrO_2 composite with enhanced electron mobility of the electroactive substance on the electrode surface and high catalytic activity.

2.5 Two-step interface self-assembly method

Separating the preparation of graphene thin films from transition metal oxide nanofilms, and subsequently transferring them to the same substrate for composite nanosheet assembly, constitutes the two-step interface self-assembly method. This technique offers the benefits of swift film formation, uncomplicated preparation conditions, and, most significantly, precise control over the nanofilm's thickness and size.

He[14] et al. adopted a two-step method for preparing GMTF composite film. The MnO_2 nanosheet sample was dispersed in N-methyl-pyrrolidone (NMP) to create MnO_2 dispersion liquid, which was then mixed uniformly with deionized water and ethyl acetate before being evaporated at room temperature. On the surface of the liquid, MnO_2 nanofilm and graphene film could both be produced. With the resultant GMTF composite film, the two substances were subsequently transferred in succession onto the nickel foam sheet.

2.6 New preparation method

A comprehensive review of the literature reveals that preparation methods for transition metal oxide mixed graphene electrode materials have their own set of issues; therefore, this paper will propose a new preparation method: Introduce a small quantity of chitosan into the graphene dispersion solution in order to increase its structural stability. The transition metal oxide particles are also evenly dispersed throughout the entire solution using ultrasonic shock for 30 minutes when preparing the precursor solution. In conclusion, the aforementioned two-step interface self-assembly technique necessitates the fabrication of a transition metal oxide nano-film and a graphene film, respectively. It is subsequently transferred to the nickel sheet made of foam.

By integrating multiple approaches, this method optimizes the utilization of their respective strengths and benefits. One illustration of this is the enhancement of stability in graphene through an amide reaction involving a minute quantity of chitosan and a surface functional group.[15]. The quality of transition metal oxide nanoparticles can be enhanced by achieving a more uniform distribution of precursor solution nanoparticles via ultrasonic shock;

furthermore, the interspersion of transition metal oxide nanosheets between graphene layers creates a two-step final rule: a complex three-dimensional structure that is more conducive to electron transport, thereby improving ion conductivity; and by mitigating the stacking issue of graphene materials, it improves capacitance.[14]

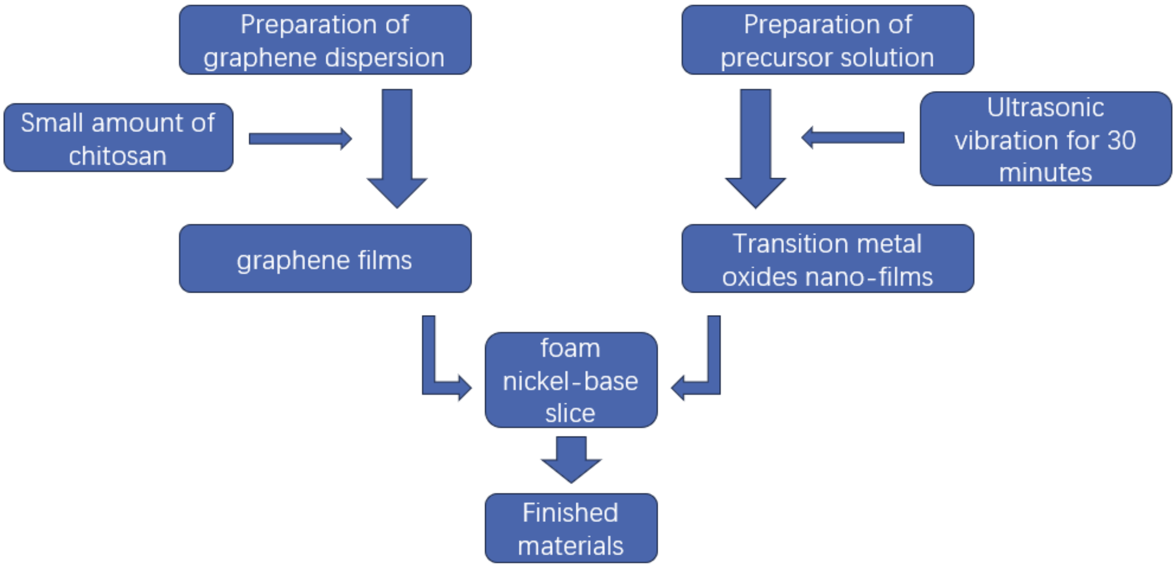

Figure 2-2 Novel preparation method

3. Application of transition metal oxide mixed graphene electrode materials in supercapacitors

As science and technology advance, there is an increasing demand for wearable electronic products. To meet this demand, wearable electronic devices need to have flexible and bendable energy storage devices that are portable and have braided performance[6]. Consequently, researchers are focusing on developing flexible wearable supercapacitors that are based on flexible electrodes and solid electrolytes. The structure of the flexible solid supercapacitor is mainly a two-dimensional sandwich structure, as shown in Figure 3-1, which is composed of flexible electrode, solid electrolyte, diaphragm and flexible packaging film[16]. The primary distinction between flexible solid-state supercapacitors and conventional capacitors lies in their utilization of flexible electrodes with enhanced flexibility and solid electrolytes with superior leak-proof safety. This design is particularly well-suited for wearable electronic devices. However, the drawback of these supercapacitors is their low energy density, which hinders their practical application.

The advancement of flexible solid supercapacitors primarily centers around enhancing the design of the solid electrolyte and flexible electrode. The progress in solid electrolyte development primarily involves the utilization of gel electrolyte to enhance the low ionic conductivity of the initial solid electrolyte. For example, Wei[17] et al. developed a gel electrolyte ZS/GL/AN using PAM, $ZnSO_4$, glycerol and acetonitrile, which not only enhanced the specific capacitance of the device assembled with ZS/GL/AN, but also greatly improved its cycle stability and freeze resistance.

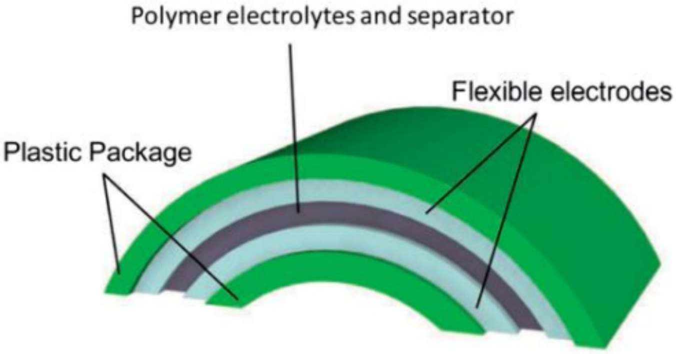

Figure 3-1 Schematic diagram of the flexible solid-state supercapacitor[16]

Compared with solid electrolytes, the number and types of flexible electrodes are more abundant, especially carbon nanomaterials and transition metal oxides. Carbon nanomaterials possess exceptional electrical conductivity and a significant specific surface area, resulting in highly stable performance. However, they are prone to agglomeration and other issues that reduce their specific surface area below the theoretical value. The use of carbon nanomaterials, such as graphene, in combination with transition metal oxides to create mixed electrode materials has gained significant attention due to the common drawbacks associated with transition metal oxides, including low conductivity, short cycle life, and easy agglomeration. The graphene material and transition metal oxide composite typically enhances the electrode structure, mitigates the agglomeration of transition metal oxide, and enhances conductivity[18]. For example, Yang et al. used NWs//MnO_2 as a positive electrode and NT//Fe_2O_3 as a negative electrode for an asymmetric supercapacitor. While maintaining a high power density of 139.1mWh/cm^3, the energy density can still reach 0.32mWh/cm^3, and it can maintain a cycle life[19].

3.1MnO_2 mixed graphene electrode material

In the synthesis of composite electrode materials incorporating graphene, MnO_2 is a prevalent transition metal oxide due to its low cost, high yield, and high theoretical specific capacity. When employed as an electrode material in a supercapacitor, MnO_2's low conductivity severely restricts the electron migration rate, resulting in a negligible amount of MnO_2 participating in the reaction and a low utilization rate. The graphene composite facilitates a greater quantity of nucleation sites for MnO_2, resulting in more uniform growth and a larger crystal nucleus, due to the three-dimensional folding structure of graphene. In order to facilitate the entry of the electrolyte and hasten the migration of electrons, the electrode material can form a loose porous structure. Similar to how the exceptional pseudocapacitance characteristics of the MnO_2 composite significantly enhance the specific capacitance of graphene.

On the contrary, the practical graphene material deviates significantly from its ideal state, resulting in numerous structural defects. In regions with a high defect density within the graphene, a considerable quantity of MnO_2 nucleate simultaneously, leading to the formation of localized agglomerations that ultimately crystallize into spherical MnO_2. A reduction in the utilization rate of MnO_2 occurs due to the inability of some of these species to participate in the reaction.. Yang[20] et al. prepared the MnO_2/G/Ni electrode material by electrodeposition under the condition of low current (0.04A). The low use current results in a substantial thickness of graphene and a limited presence of defects, facilitating the uniform deposition of MnO_2, which subsequently crystallizes into a three-dimensional linear structure. The scanning speed is $0.4A\cdot g^{-1}$, and the specific capacity is $219.3F\cdot g^{-1}$. When the scanning speed is increased to $6.4A\cdot g^{-1}$, the mass specific capacity is $115.2F\cdot g^{-1}$, and the capacity retention rate is 52.5%.

3.2Fe_2O_3 mixed graphene material

Fe_2O_3 particles exhibit superior light-shading properties when combined with graphene materials, making them more prevalent than MnO_2 in certain fields. However, Fe_2O_3 exhibits the inherent drawback of having a low ionic conductivity, a characteristic commonly observed in transition metal oxides. Additionally, the electrode structure is susceptible to damage caused by the volume effect resulting from the continuous release of ions during the charge and discharge process. Consequently, this leads to a reduction in the battery's cycle life and capacity. Upon combining the graphene material with Fe_2O_3, the ionic conductivity is enhanced, and the presence of the stable graphene structure aids in preserving the particle spacing and mitigating the effects of volume expansion. Tang[21] et al. prepared the Fe_2O_3 nanoparticle/multilayer graphene composite by water bath method. The utilization of multilayer graphene resulted in a uniform and compact material structure due to its strong interaction force with Fe_2O_3. This material exhibited exceptional performance in cyclic testing, achieving a specific discharge capacity of $1344mAh\cdot g^{-1}$ at 0.1C. Following 100 cycles, the specific discharge capacity remained at $1071mAh\cdot g^{-1}$, with a remarkable capacity retention rate of 79.7%.

3.3V_2O_3 mixed graphene electrode material

Due to the fact that V_2O_3's specific capacitance and cycle stability are relatively low in comparison to other transition metal oxides, its practical implementation in supercapacitors is infrequent. Nevertheless, through the formation of a composite material consisting of graphene and V_2O_3, the graphene material can assume the role of an elastic buffer layer on the electrode, thereby mitigating the structural strain experienced by V_2O_3 throughout the carbonization procedure and enhancing its electrical conductivity. In addition, Ling[10] et al. propose that V_2O_3 and graphene composites are designed into a layered hollow structure to prepare the hollow V_2O_3/ carbon nanospheres (H-V_2O_3/C) integrated electrode, which has a specific capacitance of 708.6 and $265.1F\cdot g^{-1}$ at 1 and $100A\cdot g^{-1}$, respectively. After 10000 cycles, the specific capacitance still maintains 98.39% of the initial value, and the supercapacitor assembled by this electrode has a wide voltage window of $2.4V^{-1}$, and can reach an ultra-high energy density of 96.8Wh·kg at a power density of $1204.6W\cdot kg^{-1}$. The reason for this is that the layered structure enhances the electrode material's specific surface area and energy density, while the hollow structure provides a greater number of electroactive sites for the charge-discharge process, thereby reducing the ion transport distance.

4. Summary and prospect

This paper provides a comprehensive overview of the recent advancements in the field of mixed materials incorporating transition metal oxides and graphene. Additionally, it outlines the various techniques utilized in the preparation of transition metal oxide scaffold electrode materials. Achieving a combination of transition metal oxides and graphene materials offers potential solutions to address several challenges associated with transition metal oxides, including their poor cycle stability, reduced specific surface area resulting from graphene agglomeration, and enhanced conductivity. These improvements could ultimately contribute to the maintenance of power density and the augmentation of energy density in supercapacitors. Due to this, the investigation into mixed graphene electrode materials containing transition metal oxides is crucial for the development of flexible solid-state supercapacitors in practice. Society is becoming increasingly interested in a variety of new energy storage equipment and is anticipating the design and development of flexible electrodes and other supercapacitors that are more portable, safer, have a higher energy and power density, and have improved cycle stability. Eventually, these demands will be satisfied. Nevertheless, the investigation of transition metal oxide mixed graphene electrode materials continues to face numerous obstacles:

(1) While the techniques for fabricating diverse powerful transition metal oxide mixed graphene electrode materials are straightforward and expeditious, they are solely adequate for laboratory-scale preparation. In practical implementation, numerous technologies are impracticable in large-scale industrial production as a result of the intricate environment and challenging-to-control variables;

(2) Despite the fact that the supercapacitor constructed from the specific transition metal oxide capacitance window material has a high energy and energy density, attempts to further enhance its electrode will be constrained by a number of factors, such as the hydrolysis of the electrode caused by excessive voltage. This indicates that further investigation is required to comprehend the synergistic mechanism between transition metal oxide mixed graphene electrode materials and other components of supercapacitors when additional variables are present;

(3) The majority of previous research on mixed graphene electrode materials incorporating transition metal oxides has concentrated on modifying the microstructure through preparation method adjustments, such as the synthesis of porous and hollow structures to increase electrochemical reactivity and specific surface area. However, there is a scarcity of studies that investigate direct modifications to transition metal oxides or graphene.

(4) The ability to precisely manipulate the structure and morphology of electrode materials has become feasible with the advancement of laser and other technologies. Future researchers will be keenly interested in determining how to alter the aperture and morphology of transition metal oxide mixed graphene electrode materials in order to affect their electrochemical performance..

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