Preparation and Properties of Carbon-based Metal Oxide Composite Electrode Materials

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Abstract: The development of new energy technology has become an important means to solve the traditional energy crisis and protect the environment[1,2]. Compared with traditional energy storage devices,supercapacitors have the advantages of high specific capacitance, fast charge and discharge, green environmental protection and excellent cycle stability[3-5]. Therefore, supercapacitors have a broad space for development in the fields of industry, equipment and transportation[6].

Transition metal oxides have typical pseudo-capacitance behavior, which depends on reversible redox reaction and chemical adsorption/desorption process to store charge[7]. However, transition metal oxides have some disadvantages such as poor conductivity and poor cycle stability. A large number of studies have shown that the composite of transition metal oxides and carbon materials is an effective way to solve the above problems[8].

This paper focuses on the application of carbon-based metal oxide electrode materials in supercapacitors. Carbon-based metal oxide electrodes were prepared by microwave hydrothermal method and their pseudo-capacitance properties were studied. $MgCo_2O_4$ crystal was synthesized by microwave-assisted hydrothermal method and subsequent calcination process. The effect of microwave reaction time on the crystal structure and morphology of $MgCo_2O_4$ was investigated. Carbon nanotubes were compounded with $MgCo_2O_4$ by hydrothermal method, and their electrochemical properties were tested. The results show that the electrode has excellent pseudo-capacitance properties and good cycle stability.

Keywords: Metallic Oxide;MgCo2O4;Carbon Nanotubes;Hydrothermal Method; Electrochemical Performance

1. Introduction

The development of science and technology not only brings convenience to mankind, but also brings a variety of arduous challenges to the environment of the earth and the survival of human beings. Especially in recent decades, the rapid development of science and technology has led to a large amount of energy consumption, and the extensive use

of non-renewable resources has made human beings face a huge crisis of energy shortage[9]. The development and effective use of renewable resources and green energy has become an urgent task for scientists to solve the energy problem. Efficient storage and conversion of energy plays a vital role in solving energy problems.

Traditional energy storage equipment has some shortcomings, such as small capacitance, slow charging and discharging speed and low service life[10]. With the rapid development of technology, more and more strict requirements are put forward for energy storage equipment, and traditional energy storage equipment can not meet the current technical needs day by day[11]. The discovery and development of supercapacitors provide a new way of thinking for energy storage. Supercapacitors have the advantages of high specific capacity, wide working temperature limit, green environmental protection, long service life and good stability. Compared with other energy storage devices, the charge and discharge of supercapacitors can be completed in an instant, a cycle can be completed in a few seconds or minutes, and a good capacity can be maintained after many cycles of charge and discharge[12].

According to the energy storage mechanism, supercapacitors are generally divided into two types: electric double-layer capacitors (EDLCs) and pseudo-capacitors (PCs)[13]. The energy storage mechanism of an EDLC is based on the electrostatic interaction between the ions on the surface of the active electrode material and the electrolyte, the rapid adsorption/desorption process as shown in Figure 1a. The energy storage mechanism of PCs transfers electrons directly through the redox reaction, there is a Faraday process, and the charge storage (capacitance) is produced by the charge transfer between the electrolyte and the electrode, similar to a battery,its principle is shown in Figure 1b[14].
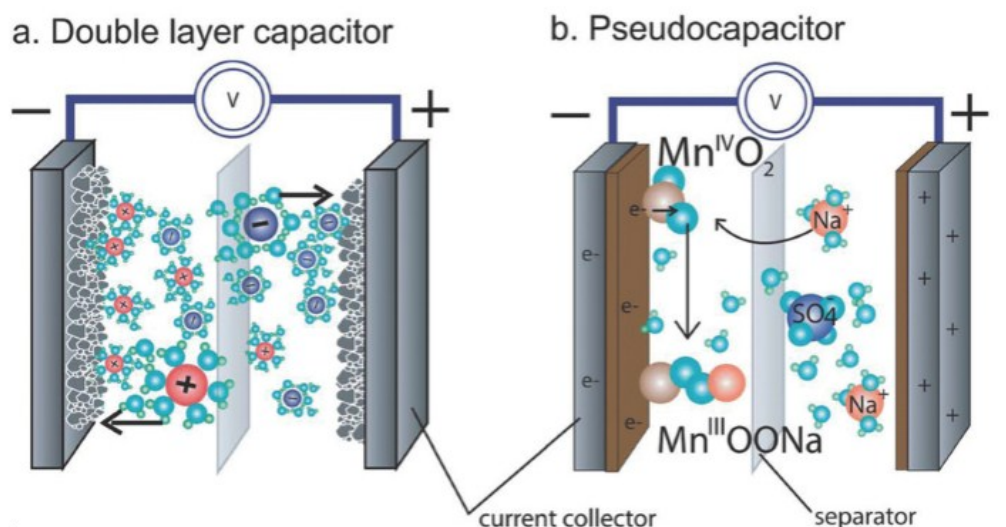

Figure 1 (a–b) Basic schematics for electrochemical double-layer capacitor (EDLC) and pseudocapacitor. Reproduced with permission[14].

Electrode materials play a decisive role in the comprehensive performance of supercapacitors, so it is particularly important to improve the performance of electrode materials. Electrode materials are roughly divided into three categories: transition metal materials0carbon materials and conductive polymer materials.

Transition metal electrode material has the advantages of ideal capacitance behavior, high specific capacitance, abundant raw materials and environment-friendly, so it is a good pseudo-capacitor material, but its rate performance and cycle stability is poor. Carbon electrode materials have excellent cycle stability, large specific surface area and many active sites, so they have high specific capacitance. However, the specific capacitance and energy density of the original carbon materials are limited, so it is necessary to obtain higher energy density through complex design. Figure 2 presents a Ragone plot of some of the composite materials compared to the performance of electrodes comprising the redox moieties alone, reveals the significant improvement that composite materials can demonstrate when properly designed[15].
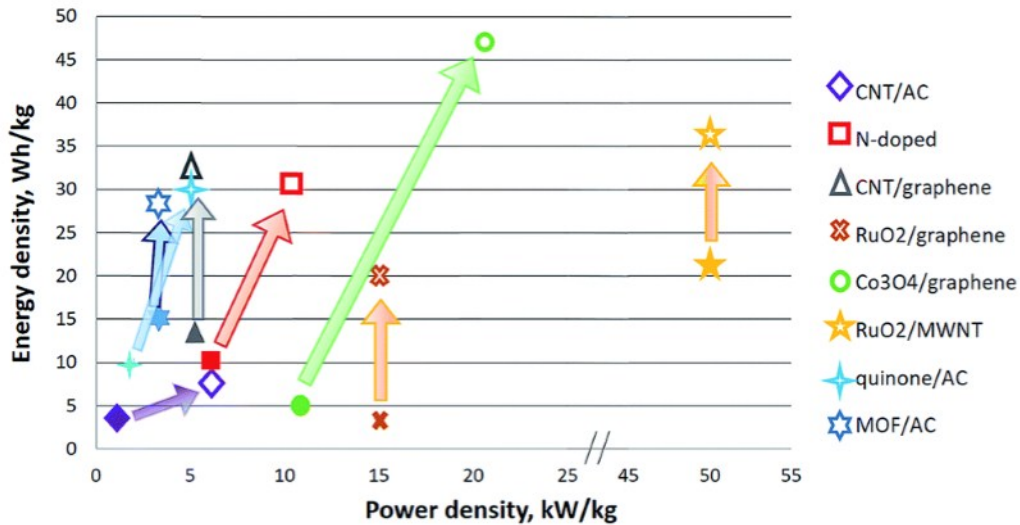

Fig. 2   Ragone plots of some representative sole redox active moieties relevant for pseudocapacitive and/or faradaic charge storage and composite electrodes comprising these moieties in composite structures with carbonaceous materials. The filled marks relate to the behavior of electrodes comprising the redox moieties as the main active mass and the unfilled marks relate to the composite materials comprising the redox active moieties with the carbonaceous matrices[15].

More and more studies have proved that the composite of carbon materials and metal oxides can effectively improve the electrical conductivity and electrochemical properties. On the one hand, carbon materials not only play a physical supporting role for metal materials in composite electrodes, but also provide a variety of channels for rapid charge transfer[16]. At the same time, in the process of high current charge and discharge, the excellent electronic conductivity of carbon materials is beneficial to the rate capacity and power density[17]. On the other hand, metal materials store charge and energy in the composite electrode, which is beneficial to the composite electrode

with the advantages of high specific capacitance and high energy density[18]. More importantly, some studies have shown that carbon materials and metal oxide composite electrodes show a synergistic effect, which is conducive to the generation of double energy storage mechanism, thus significantly improving the performance of supercapacitors[19]. In this paper, we will study the application of carbon nanotubes and nano-metal oxide composites in supercapacitors, and focus on the excellent electrochemical performance of these composite electrode materials.

2. Experimental

2.1 Introduction of metal oxide electrode material

Cobalt oxide(Co_3O_4) has high specific capacity ($3560F \cdot g^{-1}$) under ideal conditions, but it also has the shortcomings of metal oxide electrode, such as poor conductivity and cycle stability, so its performance in practical application is affected. The cobalt atoms in the cobalt oxide of a tetrahedral structure can be replaced by introducing a metal element (such as Mn, Zn, Ni and Mg in the transition system),which is easily available and with good electrical conductivity, to form a cobalt salt (MCo_2O_4,M= Mn0Fe0Co0Ni0Zn and Mg) with composite elemental oxides. Bring in other metals and forming binary oxides can not only reduce the cost, but also improve the conductivity of cobalt oxide materials, increase the reaction space, provide more and more sufficient redox reactions, greatly promote the reaction activity and progress degree, and further improve the electrochemical performance.

Cobaltate of composite phase has been widely used in many fields, such as electricity, magnetism, biological application and energy storage conversion. Among them, the outstanding performance in the field of electrochemical performance makes its application in the research of electrochemical materials widely spread. Hui[20] et al. synthesized electrode materials with multi-layered round shell shape $MnCo_2O_4$ nanoneedle morphology by direct hydrothermal method. It has a specific capacitance of $1535F \cdot g^{-1}$ at a current density of $1A \cdot g^{-1}$. When the power density is ~375 W $\cdot kg^{-1}$, the energy density reaches ~60.4 Wh $\cdot kg^{-1}$. The capacitor also has good cycle stability: it is cycled for 12000 times at 30 A $\cdot g^{-1}$, and the capacity retention rate is 94.3%. Zhang et al[21]. prepared the flower-like $NiCo_2O_4$ structure on graphene foam droplets by chemical vapor deposition and electrodeposition. The electrochemical properties of the composite material were studied, and the specific capacitance of the composite material reached $1402F \cdot g^{-1}$ at $1A \cdot g^{-1}$. When the current density is $20A \cdot g^{-1}$, the specific capacitance retention can still be 77.03%.

Among the binary transition metal oxides, $MgCo_2O_4$ has a higher theoretical specific capacitance ($3122F \cdot g^{-1}$). At present, the main problem in the preparation of $MgCo_2O_4$ electrode materials is that their properties are often limited by the deficiency and weakness of spatial and electrical properties. Therefore, a further synthesis route can be found, which is both convenient and economical. At the same time, the defect that can improve and improve the electrochemical performance of $MgCo_2O_4$ electrode materials is the

focus of the researchers of this kind of electrode materials. In this paper, $MgCo_2O_4$ and $MgCo_2O_4$@MWCNTs were prepared by simple hydrothermal synthesis. Then the prepared powders were characterized and analyzed by electrochemical analysis.

2.2 Preparation of MgCo₂O₄ and MgCo₂O₄@MWCNTs

1mmol $Mg(NO_3)_2$,2mmol $Co(NO_3)_2$,10mmol urea, 5mmol NH_4F and 40 mL deionized water were mixed and magnetically stirred for 1.5 h, then the hydrothermal reaction was carried out in an autoclave at 150! for 15 h,cooled to room temperature, and the meat pink product $(MgCo_2O_4)$was obtained by centrifugal washing and drying.

0.1g and 0.2g carbon nanotubes were added to the mixed solution of 1mmol $Mg(NO_3)_2$ and 2mmol $Co(NO_3)_2$ respectively and stirred by magnetic force for 1.5 h to obtain solution A. Then 10mmol urea and 5mmol NH_4F were added to the beaker and stirred for 1h to obtain solution B. The mixed solution C is obtained by slowly adding solution B to solution A and stirring at the same time. Then the mixed solution was hydrothermally reacted at 150! for 15h, and then the grayish black hard solid was obtained by centrifugal washing and drying, the powder of the product was obtained by fine grinding.

3. Test and analysis of electrochemical performance

3.1 Cyclic voltammetry test

Cyclic voltammetry tests the reaction process and mechanism of an electrochemical reaction system and the change of current under cyclic voltage. In the anodic oxidation zone, the current is positive, and the oxidation reaction of active substances takes place in the three-electrode system of the whole pseudo-capacitor electrode. The anode peak is a forward scanning process, and the oxidation reaction occurs in this local voltage range, and the current gradient changes significantly. Sometimes (the smaller the scanning speed is, the more obvious it is) there will be too much residual current at the upper limit of the voltage window, resulting in a rapid and large current surge polarization. However, this has no effect on the electron gain .and loss sites and processes of the reaction.
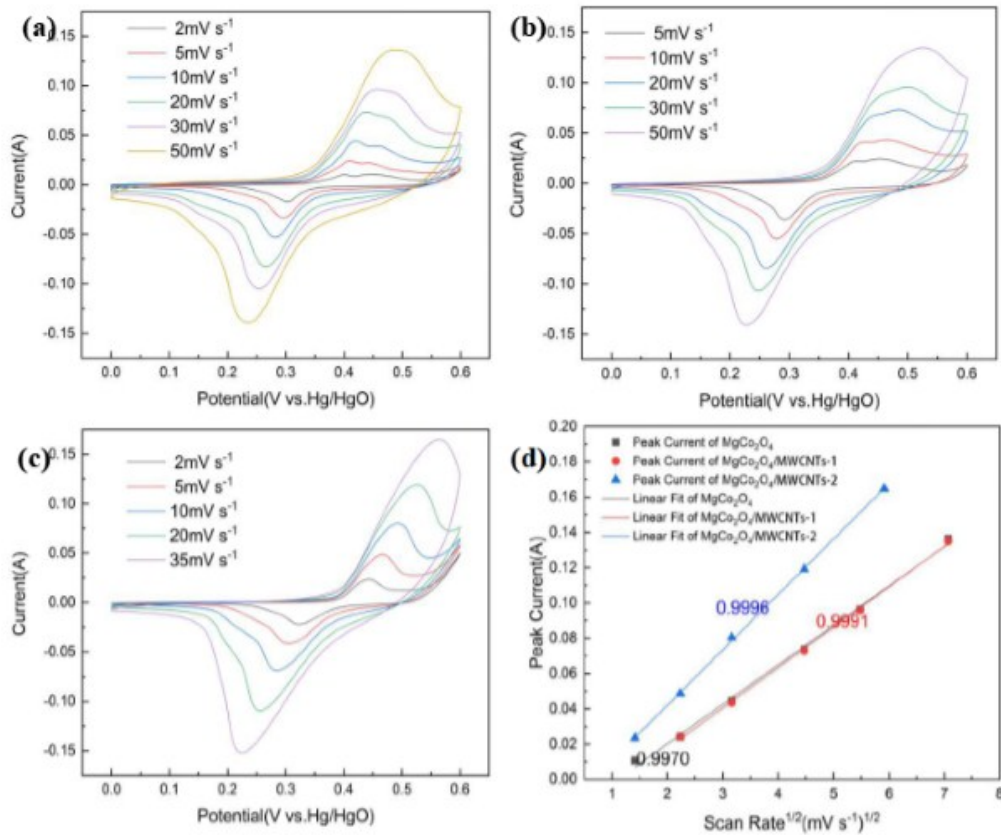
Fig. 3   **Cyclic voltammetry curve and peak current fitting graph of $MgCo_2O_4$0$MgCo_2O_4$/MWCNTs-10$MgCo_2O_4$/MWCNTs-2**

As shown in fig 3, the anode peak potentials of the three substances are all distributed between 0.36V and 0.56V, and the position relationship of the same group of anode peaks under the same scanning speed condition is E_{pa} ($MgCo_2O_4$) < E_{pa} ($MgCo_2O_4$/MWCNTs-1) <E_{pa} ($MgCo_2O_4$/MWCNTs-2). This shows that the potential required for oxidation reaction increases with this trend, and obvious double peaks are found in the forward scanning process of the first two substances at medium and low scanning speeds, indicating that there are two obvious oxidation reaction sites and reactions in this process, which confirms the conclusion that there are many valence states of Co in xps analysis. In the oxidation zone of the same substance, with the increase of scanning speed, the peak potential gradually increases and shows a single peak trend, and the peak gradually flattens until it disappears. This trend is more obvious in the two compounds, which shows the influence of scanning speed on the reactivity. In the reduction zone, that is, the negative sweep process with negative current, the basic interval of the cathode peaks of the three substances is the same and there is no obvious difference among the substances. The cathode peak of the same substance goes from about 0.3V to 0.2V with the increase of sweep speed, which is consistent with the law of substances. Looking at the change of current corresponding to the same scanning speed,

the peak current presents the trend of $E_{pa}(MgCo_2O_4) \sim E_{pa}(MgCo_2O_4/MWCNTs\text{-}1) <$ $E_{pa}(MgCo_2O_4/MWCNTs\text{-}2)$, which indicates that the current response generated in the composite 2 is the largest. The reversibility of redox reaction is judged by the symmetry of oxidation peak and reduction peak and the degree to which the peak current ratio of anode and cathode tends to 1. It can be seen from the graph that the reversibility of the three substances is very high and the graph line stability of a complete scanning cycle is also good. Looking at the fitting curve between the root values of the scanning speed of the anode peak current, the linearity of the three values is very high, and the linearity of the two compounds is infinitely tending to 1, which proves that the diffusion process and reaction progress of the composite products are very high and highly consistent with the reversible reaction process.
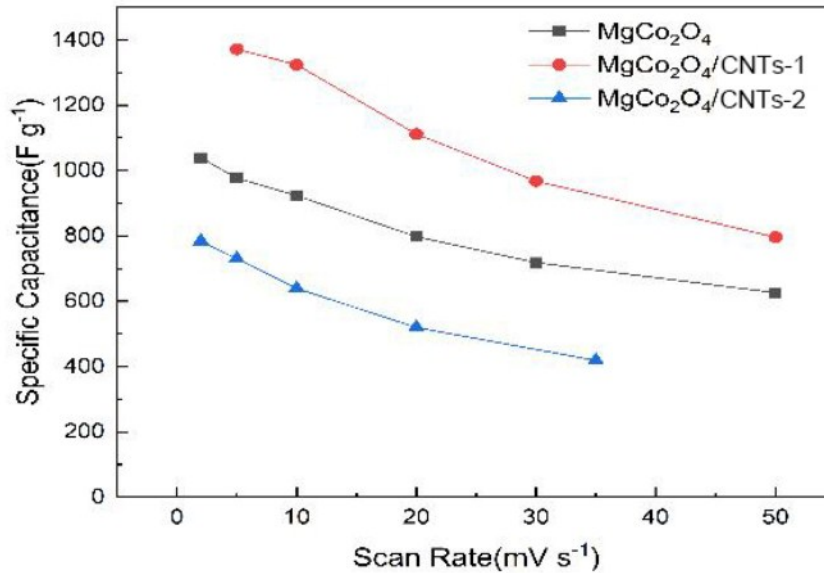

Fig.4   Specific Capacitance derived from CV curve –Scan Rate graph of $MgCo_2O_4 0 MgCo_2O_4/CNTs\text{-} 1 0 MgCo_2O_4/CNTs\text{-}2$

As shown in Figure 4, the linear relationship between the specific capacity and scanning speed calculated by cyclic voltammetry curve shows that the specific capacity of the three materials decreases slowly with the increase of scanning speed. The maximum specific volume of $MgCo_2O_4$ is $1039.1F \cdot g^{-1}$ at $2mV \cdot S^{-1}$, and the maximum specific volume of $MgCo_2O_4@CNTs\text{-}1$ is $1371.9F \cdot g^{-1}$ at $5mV \cdot S^{-1}$. The maximum specific volume of $MgCo_2O_4@CNTs\text{-}2$ is $784F \cdot g^{-1}$ at $2mV \cdot S^{-1}$. The capacity of $MgCo_2O_4@CNTs\text{-}1$ composite is larger than that of pure magnesium cobaltate and larger than that of $MgCo_2O_4@CNTs\text{-} 2$ composite, and the capacity of $MgCo_2O_4@CNTs\text{-}1$ composite also shows this relationship under other scanning speed conditions. Even at a higher scanning speed of $50mV \cdot S^{-1}$, the capacity of $MgCo_2O_4@CNTs\text{-}1$ composite still has $795.8F \cdot g^{-1}$, which implies its excellent capacity performance under this test mode. And the capacity of pure $MgCo_2O_4$ is below $30 \, mV \cdot S^{-1}$, and it also has a good capacitance of above $1000F \cdot g^{-1}$.

3.2 Test and analysis of charge-discharge performance

Figure 5 shows the test results of the galvanostatic charge-discharge ability. From the information in the figure, the electrodes of the two kinds of complexes record the time required for the electrodes to undergo a stable charge / discharge cycle between 0-0.5V voltage windows when $1A \cdot g^{-1}$, $2A \cdot g^{-1}$, $4A \cdot g^{-1}$, $6A \cdot g^{-1}$, $8A \cdot g^{-1}$ and $10A \cdot g^{-1}$ are applied with positive and negative step constant current densities from small to large, and according to the curve that the voltage changes with time.
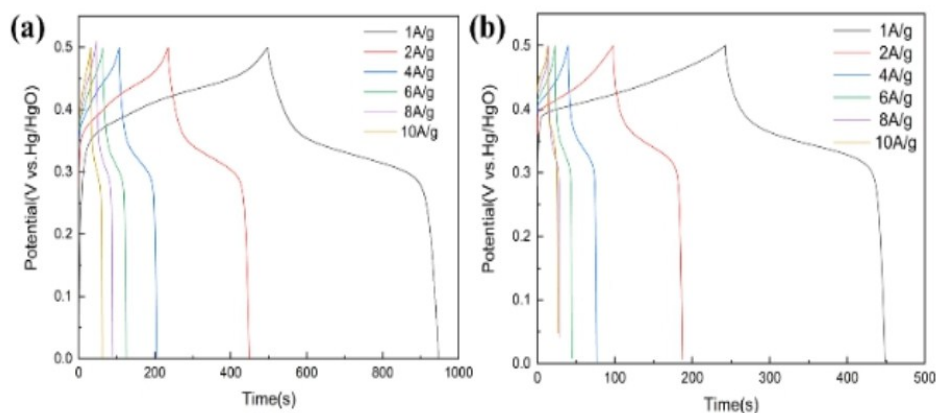

Fig 5   galvanosttic charge-discharge graph of $MgCo_2O_4/CNTs-10MgCo_2O_4/CNTs-2$

The figure 5 shows that the charging and discharging time decreases nonlinearly with the increase of current density, and both of them have the maximum charging and discharging time under the current density of $1A \cdot g^{-1}$, which indicates that under the action of small current, the voltage loading and capacity performance on the electrode are the best, and the larger the current, the obvious decline of the capacitor carrying capacity and service continuity will occur, and even the breakdown of the electrode sheet (exceeding the maximum current) will occur.

There is obviously no good performance above $5A \cdot g^{-1}$ current density. In comparison between the two compounds, it is found that the charge and discharge time of $MgCo_2O_4@CNTs-1$ compound is significantly longer than that of $MgCo_2O_4@CNTs-2$ compound at the same current density, which indicates that the specific capacity performance of $MgCo_2O_4@CNTs-1$compound electrode is better than that of $MgCo_2O_4@CNTs-2$ compound electrode. In addition, the shape of the step and sharp angle of a complete cycle pattern and the appearance potential of the platform reflect the stability and capacitance of its charge and discharge. It can be seen from the figure that the line smoothness, symmetry and jump of low current density are obvious, and the charging curve of $MgCo_2O_4@CNTs-1$ is more standard than that of $MgCo_2O_4@CNTs-2$.

On the other hand, the plateau potential of $MgCo_2O_4@CNTs-2$ was higher than that of $MgCo_2O_4@CNTs-1$ at the same current density. This shows that $MgCo_2O_4@CNTs-1$ achieves charging stage stability earlier, and the required voltage position is smaller, which also ensures its more persistent charge and discharge. The platform narrows

gradually with the increase of current density, and completely disappears when the current density reaches a certain value, at which time the charge and discharge is completely linear and the capacitance is zero.
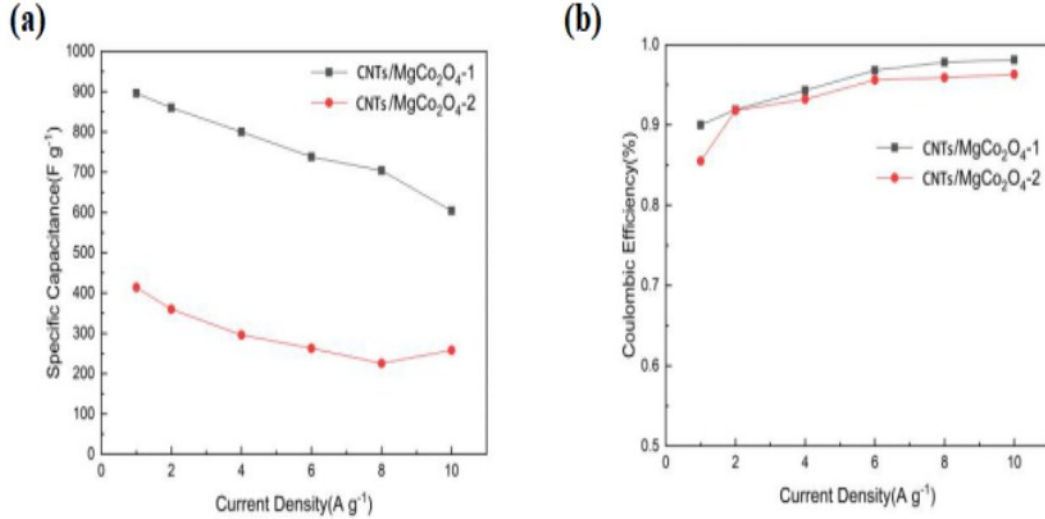

Fig 6   Specific Capacitance and Coulombic Efficiency derived from CP curves-Current density graph of $MgCo_2O_4$@CNTs-10MgCo_2O_4@CNTs-2

According to the charge and discharge curves, the specific capacitance of each material electrode and the change of Coulomb efficiency under the corresponding current density are calculated, and the corresponding current density is plotted to Figure 6, as shown in the diagram. The specific capacity of $MgCo_2O_4$@CNTs-1 is significantly greater than that of $MgCo_2O_4$@CNTs-2 at the same current density. The capacity of the two systems decreases linearly with the increase of current density, which also accords with the correlation law of electrochemical system. The calculated values are as follows:

Tab. 1 Calculation table of GCD techinique based on $MgCo_2O_4$@CNTs-1 $MgCo_2O_4$@CNTs-2

电流密度 物质	1	2	4	6	8	10
1 号	896	860	800	738	704	604
2 号	414	360	296	262.8	225.2	258

According to the data in the table, the maximum capacity of $MgCo_2O_4$@CNTs-1 is 896F·g^{-1} under 1A·g^{-1}, and its minimum specific capacity can reach that of 604F·g^{-1} under 10A·g^{-1}. The capacity of sample $MgCo_2O_4$@CNTs-2 is obviously smaller, and the maximum capacity is 414F·g^{-1} under 1A·g^{-1}. The Coulomb efficiency refers to the conversion efficiency of charging capacity during charge and discharge cycle, which reflects the advantages and disadvantages of discharge and electric energy utilization

capacity of an electrical system. The Coulomb efficiency of high performance electrochemical elements is close to 1, and the initial efficiency is small. The efficiency changes shown in Fig 6b, the efficiency changes of the two kinds of composites are consistent with the law and are good, while the Coulomb efficiency of $MgCo_2O_4$@CNTs-1 is higher than that of $MgCo_2O_4$@CNTs-2, to 98.1% of 10 A $\cdot g^{-1}$. The results show that the power conversion and performance of $MgCo_2O_4$@CNTs-1 are better.

3.3 Cycle performance

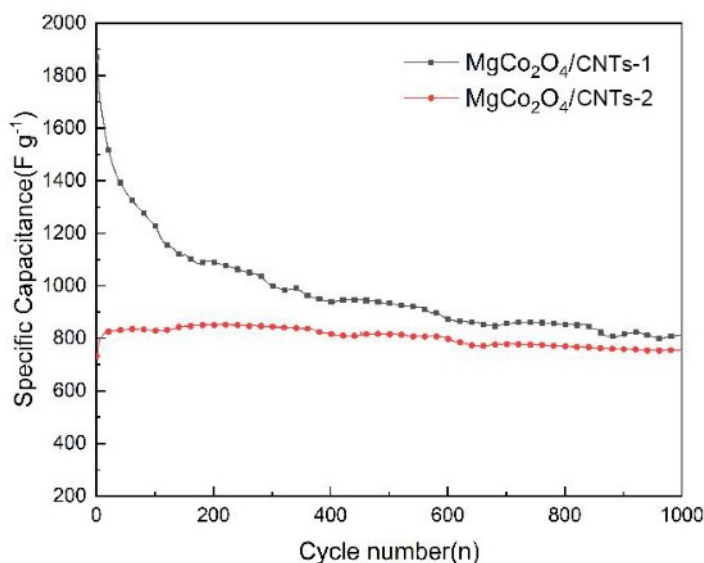Fig 7   Specific Capacitance derived from charge-discharge process after 1000 cycle of $MgCo_2O_4$@CNTs-10$MgCo_2O_{4@}$CNTs-2

Figure 7 shows the capacity change process of two kinds of complex after a thousand cycles under 1A/g current density. The cycle capacity of complex $MgCo_2O_4$@CNTs-1 shows an extremely high initial cycle capacity and a large degree of capacity attenuation, and gradually decreases steadily after about 200 cycles, which indicates that the initial capacity performance is outstanding but not stable, and the maximum cycle capacity reaches 1871.6F $\cdot g^{-1}$.

The capacity retention rate of the whole cycle is 43.4%, and the minimum capacity of the cycle can reach 811.6F $\cdot g^{-1}$.The electric curve of $MgCo_2O_4$@CNTs-2 complex fluctuates gently and the capacity attenuates slowly. The maximum capacity appears around 240 laps, which is 852.3F $\cdot g^{-1}$, while the lowest capacity in the cycle is 753.1F $\cdot g^{-1}$. This shows that the $MgCo_2O_4$@CNTs-2 material electrode has a good capacity retention (the retention rate is 88.4%), and the working stability and service life of its charge-discharge long cycle are better than those of $MgCo_2O_4$@CNTs-1. However, the overall discharge life and capacity are significantly lower than that of $MgCo_2O_4$@CNTs-1 electrode. Therefore, it is necessary to adjust the stable performance of $MgCo_2O_4$@CNTs-1 in practical application.

4. Conclusion

$MgCo_2O_4$ with nano-flower cluster morphology was synthesized by hydrothermal method. The electrochemical properties of the products were tested by adding carbon nanotubes with different mass (0.1g, 0.2g) and compounding with $MgCo_2O_4$. The results show that the reaction processes of pure $MgCo_2O_4$ and the two complexes are highly reversible, and pure $MgCo_2O_4$ and 0.1g MWCNTs composite products have obvious active sites for intermediate reactions. The CV and CP capacity of 0.1g composite products were significantly higher than that of 0.2g composite products under the same test conditions, and the maximum discharge specific capacity reached 896F·g^{-1} of 1A·g^{-1}. And the electric energy efficiency is up to 98.1%. The overall impedance performance of the $MgCo_2O_4$@CNTs-1 complex is excellent, and the impedance of each part of the complex is less than that of the $MgCo_2O_4$@CNTs-2 complex, and the overall capacity of its long cycle is significantly higher than that of $MgCo_2O_4$@CNTs-2 (the lowest cycle capacity 811.6F·g^{-1}). However, its cycling stability and retention are not as good as 88.4% at 1 A·g^{-1} current density of $MgCo_2O_4$@CNTs-2. It can be concluded that the composite products of flower-shaped $MgCo_2O_4$ and its highly conductive materials have potential electrochemical properties, and the performance of the composite of 0.1g MWCNTs and $MgCo_2O_4$ is better.

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