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# **Preparation and Electrochemical Performance of CoS<sub>2</sub>/carbon nanofibers as electrode materials for supercapacitors**

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Electrode materials are one of the core components of supercapacitors, and cobalt-sulfur compounds have the following advantages: insoluble in alkaline solutions, long service lives, high conductivities and abundant valence states. The addition of a sulfur source by the hydrothermal method can decrease the discharge of harmful gases. Influencing factors can be adjusted to prepare a composite with excellent electrochemical properties. The structural and morphological properties of CoS2/CNFs are characterized through X-ray diffraction, scanning electron microscopy, transmission electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. CoS2/CNFs reaches 380.4 F·g–1; thus, over 81.2% of the initial capacitance is retained as the current density was increased from 1 to 10 A·g–1. CoS2/CNFs also exhibits excellent cycling performance with 90.5% capacitance retention after 2000 charge/discharge cycles. The combination of CoS2 and carbon nanofibers can not only reduce volume expansion but also improve cycling stability.

Keywords: Electrospinning; CoS<sub>2</sub>/CNFs; supercapacitors; electrode; electrochemical performance

## **1. INTRODUCTION**

In our current rapidly developing society and with the increase in population, people are consuming increasing amounts of energy. At present, the energy we rely on mainly stems from fossil fuels, but fossil fuels are nonrenewable energy sources. As people's energy consumption increases year by year, the global production of energy is gradually decreasing[1]. In the process of using fossil fuels, we are faced not only with the problem of energy depletion but also with serious environmental pollution, such as haze, acid rain, and global warming [2]. Therefore, under such severe circumstances, the development of new clean energy is a global issue, which has become the research direction of an increasing number of researchers[3]. Clean energy currently being used is limited by geographical

conditions, such as sunlight availability and climate[4]. Additionally, electrochemical energy storage plays an important role in a series of energy storage systems and has a far-reaching influence due to its stable voltage and current, stable power supply long periods of time and simple preparation[5]. Supercapacitors, lithium-ion batteries and fuel cells are three main types of electrochemical energy storage systems. Supercapacitors have been increasingly studied because of their high power density, long cycling life, cleanliness and pollution-free nature[6]. Therefore, it is of great significance to prepare energy storage systems with a high energy density and power density and long cycling life to improve the current problem of energy depletion.

Electrode materials are the core components of supercapacitors[7, 8]. The generation, storage, and transfer of capacitance are all carried out on the surface of the electrode material without destroying its interior structure. At present, electrode materials can commonly be divided into carbon materials[9, 10], metal compounds[11, 12] and conductive polymers[13, 14]. As a common carbon material, carbon nanofibers are often used as electrode materials for supercapacitors due to their high electrical conductivity, stable chemical properties and abundant chemical active sites[15]. However, the common shortcoming of all carbon materials is their lack of energy density. Using electrospinning to make carbon nanofibers requires high polymers, which are expensive; thus, replacing them with other carbon materials can save costs[16]. Among all the transition metal compounds, transition metal sulfides have been a research hotspot in recent years due to having a wide range of sources along with their rich variety and low price[16]. Transition metal sulfides not only have faradaic oxidation-reduction reactions but can also exhibit electric double layer charge adsorption and desorption behavior, thus providing a higher energy density.

Cobalt-based sulfides can be used as electrode materials for supercapacitors because of their high conductivity and different stoichiometry in various transition metal sulfides, and currently, the main options are CoS[17, 18],  $CoS_2[19, 20]$ ,  $Co_3S_4[21, 22]$  and  $Co_8S_9[23, 24]$ . Although cobalt-sulfur compounds have many unique advantages, they also have their own shortcomings, such as volume expansion and rapid change during charging and discharging. These shortcomings make the active material easily fall from a nickel foam sheet, leading to a rapid attenuation of electric capacity. To solve the above problems, the following are the current solutions. First, a hollow structure can be prepared to alleviate volume expansion; thus, there is space for alleviating the change in volume during charging and discharging, which prevents the active material from falling off the nickel foam sheet[25, 26]. Second, the use of a carbon coating or the combination of cobalt-sulfur compounds with carbon materials improves the cycling stability of the resulting cobalt-sulfur compound electrode[27].

 $CoS_2$  nanoparticles can be prepared by the hydrothermal method. Hydrothermal synthesis is an effective method and approach to prepare functional new materials[28, 29]. Its main characteristics are as follows: (1) The reaction is carried out in a sealed container, which can reduce the volatilization of toxic and harmful gases, which decreases environmental pollution; (2) During the reaction process, the electrochemical properties of the prepared composite materials are adjusted by adjusting the factors that influence reaction conditions, including temperature and time. Xing [20] reported that octahedron-shaped  $CoS_2$  crystals were successfully fabricated through a simple hydrothermal route (at 160 °C for 22 h) without any surfactant or template. The as-fabricated  $CoS_2$  electrode showed typical pseudocapacitive properties with a specific capacitance of 236.5 F·g<sup>-1</sup> at 1 A·g<sup>-1</sup>. Furthermore, this

electrode exhibited excellent cycling stability at  $2 \text{ A} \cdot \text{g}^{-1}$  with only a loss of 7.4% in specific capacitance after 2000 cycles. Wang [30] reported the preparation of a CoS<sub>2</sub>-graphene nanocomposite by a facile solvothermal method (at 160 °C for 6 h). The CoS<sub>2</sub>-graphene nanocomposite exhibited a specific capacitance of 314 F  $\cdot$ g<sup>-1</sup> at a current rate of 0.5 A  $\cdot$ g<sup>-1</sup> and excellent cycling stability.

This paper discusses the influence of hydrothermal time and temperature on the electrochemical properties of the prepared composite materials. The combination of  $CoS_2$  and carbon materials can not only compensate for the shortcomings of the insufficient energy density of carbon materials but also alleviate the volume expansion of metal sulfides during charge and discharge. This combined material demonstrates a synergistic effect between the different materials, thereby significantly improving the electrochemical performance and cycling stability.

#### 2. EXPERIMENTAL

## 2.1. Experimental method

#### 2.1.1. The preparation of Co/CNFs

Firstly, 0.9 g polyacrylonitrile (PAN, molecular weight 150,000) and 0.1g carbon materials[8] were dissolved in 10 mL N, N-dimethylformamide solution, and then stirred at room temperature on a magnetic agitator. Because the solubility of porous carbon in organic solvent was not ideal, the porous carbon was suspended and evenly dispersed in the organic solution. Then 2mmol of cobalt acetate was added and stirred on the magnetic stirrer until the uniform mixture was obtained as spinning liquid. Next the spinning liquid was ultrasonic on the sonicator for 10 min to make the mixture completely uniform. The spinning fluid was sucked into a plastic syringe, connected with a 21 gauge stainless steel needle, and then connected to a high-voltage power supply with aluminum foil as the receiver. The distance between sprinkler head and receiver was 18 cm, the positive high pressure was 12 kV, the negative high was -3 kV, and the pushing speed was  $0.15 \text{ mm} \cdot \text{min}^{-1}$ . Then, the spun fiber film was placed on a magnetic boat and pre-oxidized in a muffle furnace to 260 °C for 2 h at the heating rate of  $1^\circ \text{C} \cdot \text{min}^{-1}$ . After that, the pre-oxidized film was carbonized in a tubular furnace, which was then heated to 800 °C for 1 h with a heating rate of  $5^\circ \text{C} \cdot \text{min}^{-1}$ , and naturally cooled to room temperature to obtain cobalt-based carbon nanofibers (Co/CNFs).

## 2.1.2 The preparation of CoS<sub>2</sub>/CNFs

According to the molar ratio of 1:10, thioacetamide was added to 60 mL ethylene glycol solvent and stirred on a magnetic agitator for 1 h to obtain a uniform mixture. Then the mixture was transferred to 100 mL teflon lining, and the above prepared Co/CNFs was added into the mixture, and then put into a vacuum drying oven for reaction. At the end of the reaction, after the high-pressure hydrothermal reactor was cooled to room temperature, the solvent was filtered and stirred with anhydrous ethanol on the magnetic stirrer at room temperature for 3 h. Subsequently, the resulting black solid product was washed with anhydrous ethanol and distilled water repeatedly, and finally dried in vacuum at 60 °C for 10 h. The composite prepared was named according to the hydrothermal reaction time and temperature, as shown in Table 1. The preparation flow chart is shown in Scheme1.



**Table 1.** Experimental preparation sample table

Scheme 1. Schematic illustration for preparation of CoS<sub>2</sub>/CNFs

#### 2.2. Structure characterization

The structure of the as-prepared samples was tested by X-ray diffractometer (XRD, MSA-XD<sub>2</sub>, Rigaku, Japan) in the scanning range of the diffraction angle is 5 to 80°. The Lab RAM HR Evolution microconfocal Raman spectrometer was used to analyze the samples to determine whether  $CoS_2$  was loaded into CNFs. The microstructure of composites was analyzed by cold field emission scanning electron microscope (SEM, XFlash 6130, Japan Electron Optics Co., Ltd.). The surface morphology and crystal structure of the material were analyzed by transmission electron microscopy (TEM, FEI Company, USA) and combined with XRD test results. The X-ray photoelectron spectroscopy (XPS) spectra were used to characterize the composition and structure of the surface elements on a scanning X-ray photoelectron spectrometer (Thermo Scientific, USA) with monochromatized Al K $\alpha$  X-ray source.

#### 2.3 Test of electrochemical properties.

The electrochemical performance was measured on the CHI660E electrochemical work station (CHI660E, Shanghai Chenhua Instrument Co., Ltd.) with a conventional three-electrode configuration

in 6 mol·L<sup>-1</sup> KOH solution. The prepared composite, acetylene black and polytetrafluorethylene (PTFE) were mixed uniformly with 80%, 15% and 5% mass ratios to prepare the working electrode[31]. The evenly mixed paste was coated on a  $2\times1$  cm foamed nickel sheet, covering an area of  $1\times1$  cm. The prepared working electrode was placed in a vacuum drying oven and dried at 70 °C for 12 h, and then pressed under a pressure of 5 M Pa for 40 s to make an electrode sheet. The prepared composite material, saturated mercury oxide electrode and platinum foil were used as working electrode, reference electrode and counter electrode, working electrode respectively, and cyclic voltammetry (CV), constant current charge and discharge (GCD) and impedance (EIS) tests were performed on electrochemical workstation. The cyclic voltammetry (CV) measurements were made at a scanning rate of 5 to 40 mV·s<sup>-1</sup> at a voltage range of -0.2 V-0.5 V. The constant current charge/discharge (GCD) measurements were made at a current density from 1 to 10 A·g<sup>-1</sup>, with a potential of -0.1V-0.4V. The specific capacitance C (F·g<sup>-1</sup>) was calculated using the following formulae:

 $C = \frac{I\Delta t}{m\Delta V}$ 

where idenotes the discharge current,  $\Delta t$  is the discharge time, m is the mass load,  $\Delta V$  is the potential window of discharge[32, 33].

## **3. RESULT AND DISCUSSION**

## 3.1 SEM and TEM analysis of CoS<sub>2</sub>/CNFs.

In order to study the composition of CoS<sub>2</sub> and carbon nanofibers from the perspective of microscopic characterization, SEM and TEM tests were carried out on CoS<sub>2</sub>/CNFs, and the results are shown in Figure 1. Figure 1a shows the thin film after electrostatic spinning. The fiber is evenly distributed and the surface is smooth, indicating that cobalt ions have completely dissolved into the fiber. Figure 1b shows the scanning electron microscope (SEM) of the carbonized Co/CNFs nanofiber. It can be seen from the figure that there are fine particles attached on the surface of the fiber and they are uniformly distributed on the surface of the carbon nanofiber, indicating that the cobalt ions do not agglomerate. As can be seen from the Figure 1c, the particles on the CoS<sub>2</sub>/CNFs composite materials after hydrothermal sulfidation increased significantly. This is because in the process of hydrothermal reaction, sulfur ions in thioacetamide are dissociated due to high temperature and combine with cobalt ions on carbon nanofibers to form CoS<sub>2</sub>. In the sulfidation process, the volume expands and destroys the carbon fibers, thus appearing on the surface of the fibers. Moreover, it can be seen from the TEM images (Figure 1d and Figure 1e) of the CoS<sub>2</sub>/CNFs composite materials that CoS<sub>2</sub> is uniformly distributed on the surface of the carbon nanofibers instead of agglomerating together. So carbon nanofibers effectively prevent CoS<sub>2</sub> from coalescing. Figure 1f is the HRTEM of CoS<sub>2</sub>/CNFs composite materials. The HRTEM image of CoS<sub>2</sub>/CNFs composite materials shows a lattice spacing of 0.167 nm, which is consistent with the (311) crystal plane of  $CoS_2$ .



- Figure 1. (a) SEM image of PAN-based carbon nanofibers; (b) SEM image of Co/CNFs composite material; (c) SEM image of CoS<sub>2</sub>/CNFs composite materials; (d) TEM image of CoS<sub>2</sub>/CNFs composite materials; (f) HETEM diffraction ring diagram of CoS<sub>2</sub>/CNFs composite materials.
- 3.2 XRD analysis of CoS<sub>2</sub>/CNFs.

In order to verify the crystal structure of the composite, the XRD analysis of the composite was carried out.



Figure 2. XRD patterns of CoS<sub>2</sub>/CNFs.

As can be seen from the Figure 2, compared with the standard pattern of JCPDSNo.41-1471 the diffraction peaks appear near  $2\theta$ =27.9°, 32.3°, 36.2°, 39.8°, 46.3°, 54.9° and 60.4° corresponding to crystal surfaces of CoS<sub>2</sub> (111), (200), (210), (211), (220), (311) and (230) respectively[20, 34]. In the XRD pattern of the CoS<sub>2</sub>/CNFs composite material, it can be seen that there is a peak near 23° corresponding to the (002) crystal plane of the graphite layer, which can prove that the prepared composite material contains carbon material and CoS<sub>2</sub>[31].

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#### 3.3 Raman spectrum analysis of CoS<sub>2</sub>/CNFs.

In order to further verify whether the CNFs and  $CoS_2$  were combined or not, we carried out Raman test on  $CoS_2/CNFs$  composite materials. There is a diffraction peak near 670 cm<sup>-1</sup>, which belongs to the characteristic peak of cobalt ion in  $CoS_2$ , as shown in Figure 3[35]. At the same time, two obvious characteristic peaks were observed near 1353 cm<sup>-1</sup> and 1585 cm<sup>-1</sup>, which belong to D peak and G peak in carbon materials, thus further indicating the successful composite of  $CoS_2$  and CNFs. The D peak represents the disordered structure of the carbon material, while G peak represents the graphitized structure, and the value of  $I_D/I_G$  is commonly used to analyze the graphitization degree of the carbon material is 1.06, indicating that  $CoS_2$  has a small degree of graphitization damage to the composite material.



Figure 3. Raman spectrum of the CoS<sub>2</sub>/CNFs.

## 3.4 XPS elemental analysis of CoS<sub>2</sub>/CNFs.

In order to further characterize the phase composition of  $CoS_2/CNFs$  composite materials, we analyzed the binding energy and chemical morphology of the composite materials through the XPS test, as shown in Figure 4. Figure 4a shows the full peak spectrum of the  $CoS_2/CNFs$  composite materials. It can be seen from the figure that the  $CoS_2/CNFs$  composite materials contains four elements including C, O, Co, and S. Among them, the C element is provided by the prepared carbon material and polymer polyacrylonitrile (PAN) as the carbon source; the O element is introduced after spinning and pre-oxidation in the muffle furnace under air atmosphere. The purpose of pre-oxidation in muffle furnace is to enhance the toughness of carbon nanofibers. The Co and S elements are added during the experiment.



**Figure 4.** XPS of CoS<sub>2</sub>/CNFs. (a) Full spectrum; (b) C 1s energy spectrum; (c) O 1s energy spectrum; (d) Co 2p energy spectrum; (e) S 2p energy spectrum.

The C 1s has four fitting peaks (Figure 4b), which are located near 284.7eV, 284.9 eV, 286.4 eV and 288.6 eV, respectively corresponding to C=C-C, C-S, C-O and C=O. The presence of C-S means that some of the sulfur ions are embedded in the lattice of the carbon[15]. For O1s (Figure 4c), the CoS<sub>2</sub>/CNFs composite materials can be divided into three parts, which are located near 531.6 eV, 532.7 eV, 533.7 eV respectively corresponding to C=O, C-O and O=C-O[9]. Figure 4d shows the fitting peak of the Co 2p element in the composite materials. The Co 2p spectrum can be fitted with six peaks, and the binding energies of Co  $2p_{3/2}$  and Co  $2p_{1/2}$  are 776.1 eV to 790.4 eV and 792.9 eV to 808.3 eV, respectively[36]. For the S 2p, as shown in Figure 4d, the characteristic peak at 162.5 eV is due to the presence of S<sup>2-</sup> dimer in the composite. Meanwhile, a small characteristic peak at 168.5 eV, which is a peak formed by the O-S bond. This may be due to the partial formation of sulfur oxide on the surface of the material as oxygen is absorbed[37]. The content of element in CoS<sub>2</sub>/CNFs composite materials is shown in Table 2. It can be seen from Table 2 that Co: S is 2.96%6.18%, close to 1:2, which further proves that CoS<sub>2</sub> is formed, which is consistent with XRD and Raman analysis results.

Table 2. Surface element content of CoS<sub>2</sub>/CNFs

Sample	С %	O %	Fe %	<b>S%</b>
CoS <sub>2</sub> /CNFs	71.33	19.53	2.97	6.18

#### 3.5 Electrochemical properties.

Hydrothermal temperature is the main factor affecting the reaction. Under the condition of hydrothermal time of 12 h, the influence of hydrothermal temperatures of 120 °C, 150 °C and 180 °C on the electrochemical performance of the composite material are discussed respectively, as shown in Figure 5.



**Figure 5.** Electrochemical properties of composite materials at different hydrothermal temperatures: (a) cyclic voltammetry diagram at 30mV·s<sup>-1</sup>; (b) constant current charge-discharge diagram at 1 A·g<sup>-1</sup>; (c) AC impedance chart; (d) specific capacitance versus current density Change diagram.

Figure 5a shows the CV of different hydrothermal temperatures at scan rate of 30 mV·s<sup>-1</sup>. It can be seen from the figure that the composites prepared under different hydrothermal temperatures have a pair of obvious redox peaks, which are the redox reactions of cobalt metal ions in the electrolyte[38]. The cyclic voltammograms of the CoS<sub>2</sub>/CNFs-2 have the largest area and the best electrochemical

performance. As can be seen from the Figure5b, the composite materials prepared at different hydrothermal temperatures have a platform during the charging and discharging process, so the relationship between the charging and discharging time and voltage is no longer linear, but shows a significant slope change, which is consistent with the redox peak on the cyclic voltammetry curve[39]. At the current density of  $1A \cdot g^{-1}$ , the specific capacitance of theCoS<sub>2</sub>/CNFs-1, CoS<sub>2</sub>/CNFs-2, CoS<sub>2</sub>/CNFs-3 are 304.2 F  $\cdot g^{-1}$ , 331.0 F  $\cdot g^{-1}$  and 266.8 F  $\cdot g^{-1}$  respectively. The charge and discharge time of CoS<sub>2</sub>/CNFs-2 is the longest and the specific capacitance is the best.

Figure 5c is the AC impedance diagram of different hydrothermal temperatures. As can be seen from the figure,  $CoS_2/CNFs$ -2 has the highest slope and the lowest internal resistance. Figure 5d shows that the specific capacitance of the load materials prepared at different hydrothermal temperatures decreases with the increase of current density. This decrease in capacitance can be due to the active molecules in the electrode materials cannot fully contact with the electrolyte at a high current density, thus reducing the energy storage speed[40]. When the current density increases by 10 times ( $1 \text{ A} \cdot \text{g}^{-1}$  to  $10 \text{ A} \cdot \text{g}^{-1}$ ), the capacitance retention rates of  $CoS_2/CNFs$ -1,  $CoS_2/CNFs$ -2,  $CoS_2/CNFs$ -3 are 77.1%, 78.7% and 75.7% respectively. To sum up, the  $CoS_2/CNFs$ -2 composite has the best electrochemical performance. If the hydrothermal temperature is too low, the sulfur ions in the thioacetamide cannot be sufficiently freed to combine with the cobalt ions on carbon nanofibers, resulting in less metal sulfides, which leads to poor electrochemical performance. When the temperature is too high, although the sulfur ion completely dissociates, it is rapidly decomposed into the organic solvent ethylene glycol solution, which leads to the poor binding effect of cobalt metal ion and sulfur ion.

The hydrothermal time is another major factor affecting the reaction. Under the hydrothermal temperature of 150 °C, the effects of hydrothermal time of 9 h, 12 h and 15 h on the electrochemical properties of the prepared composite materials are discussed(Figure 6). It can be seen from Figure 6a that there is a pair of obvious redox peaks, which occur because of the redox reaction between cobalt metal ions and ions in the electrolyte. At the same sweeping speed ( $30 \text{ mV} \cdot \text{s}^{-1}$ ), the composite prepared under different hydrothermal time all have a pair of obvious redox peaks, indicating that the composite electrode material prepared play a dominant role of pseudocapacitance[41].The CoS<sub>2</sub>/CNFs-2 composite material has the maximum curve integral area and the specific capacitance.





Figure 6. Electrochemical properties of composites with different hydrothermal times: (a) cyclic voltammetry diagram at 30 mV·s<sup>-1</sup>; (b) constant current charge-discharge diagram at 1 A·g<sup>-1</sup>; (c) AC impedance chart; (d) specific capacitance versus current density Change diagram.

There is a platform for different hydrothermal times in the charging and discharging process, which corresponds to the redox peak in the cyclic voltammetric diagram, as shown in Figure 6b. At the current density of 1 A·g<sup>-1</sup>, the specific capacitance of the CoS<sub>2</sub>/CNFs-4, CoS<sub>2</sub>/CNFs-2, CoS<sub>2</sub>/CNFs-5 are 308.0  $\text{F} \cdot \text{g}^{-1}$ , 331.0  $\text{F} \cdot \text{g}^{-1}$  and 202.0  $\text{F} \cdot \text{g}^{-1}$  respectively. The charge and discharge time of CoS<sub>2</sub>/CNFs-2 is the longest and the specific capacitance is the best. The charge and discharge time of  $CoS_2/CNFs-2$ composite material is the longest, which indicates that the electrochemical performance of composite material prepared under that condition is the best. Figure 6c is the AC impedance diagram of different hydrothermal time. As can be seen from the figure, CoS<sub>2</sub>/CNFs-2 has the highest slope and the lowest internal resistance. Figure 6d shows that the specific capacitance of the composite material prepared at different hydrothermal times decreases as the current density increases. As the current density increases in supercapacitors, it is a common phenomenon that the specific capacitance decreases. This is because the active molecules in the electrode materials can fully contact with the electrolyte at a small current density, thus sufficiently generating oxidation-reduction reaction[42]. Therefore more energy is stored on the electrode material surface. When the current density increases, the active molecules do not have sufficient contact with the electrolyte, so that rapid energy storage cannot be carried out. When the current density increases by 20 times (0.5  $A \cdot g^{-1}$  to 10  $A \cdot g^{-1}$ ), the capacitance retention rates of CoS<sub>2</sub>/CNFs-4, CoS<sub>2</sub>/CNFs-2, CoS<sub>2</sub>/CNFs-5 are 75.5%, 78.2% and 64.5% respectively. In summary, the CoS<sub>2</sub>/CNFs-2 composite has the best electrochemical performance. When the hydrothermal time is too short, the thioacetamide in the reaction system cannot be completely separated, resulting in the low concentration of sulfur atoms in the reaction system, which affects the growth rate of metal sulfides. If the hydrothermal time is too long, the metal sulfides that have been bound to the carbon nanofibers disintegrate into organic solvents and are filtered out, resulting in a decrease in the specific capacitance.

Therefore, under the hydrothermal temperature of 150 °C and hydrothermal time of 12 h, the composite prepared has the excellent electrochemical performance. There will be amorphous carbon in the composites prepared by hydrothermal reaction. The sulfuretted composites were annealed at 500 °C for 1 h in a tubular furnace. It can be seen from the Figure7 that the electrochemical properties of the composite prepared after annealing increase, indicating that low temperature annealing can remove the

amorphous carbon on the surface of the composites and improve the electrochemical performance of the composites. The annealed composite was named  $CoS_2/CNFs$ .

The electrochemical test of  $CoS_2/CNFs$  composite was performed below, as shown in Figure 8. At different scanning speeds (5-40 mV·s<sup>-1</sup>), there is a pair of redox peaks, instead of the ideal rectangular double-layer, indicating that  $CoS_2/CNFs$  composite material is not simply electrostatic charge adsorption and ion diffusion, but shows the electrochemical performance of pseudocapacitance, as shown in Figure 8a. When the scanning velocity was increased to 40 mV·s<sup>-1</sup>, significant redox peaks could still be observed. However, polarization occurs, which may be due to ohmic voltage drop and dispersion capacitance effects at large scanning speeds. In addition, when the scanning rate increases from 5 to 40 mV·s<sup>-1</sup>, the position of the redox peak is shifted. That is because the redox reaction cannot satisfy the electron neutralization, which limits the diffusion rate of ions[43]



**Figure 7.** Before and after  $CoS_2/CNF$  annealing. (a) CV curves at a scan rateof $20mV \cdot s^{-1}$ ; (b) GCD curves at the current density of 1  $A \cdot g^{-1}$ ; (c) Electrochemical impedance spectra (EIS); (d) Specific capacitance of the samples versus various current densities from 1 to  $10 A \cdot g^{-1}$ .

At present, the electrochemical reaction mechanism of metal sulfide in the alkaline electrolyte is not particularly clear, but the element sulfur and oxygen belong to the same race. Therefore referring to the Faraday reaction of metal oxide in the alkaline electrolyte, it is inferred that the redox reaction of  $CoS_2/CNFs$  composite material as the electrode material in KOH electrolyte[15, 43, 44]:

$$CoS_2 + OH^{-=}CoS_2OH + H_2O + e^{-1}$$

$$CoS_2OH + OH^{-=}CoS_2O + H_2O + e^{-1}$$

$$3$$

Figure 8b shows the relationship between the peak current and the square root of the scan rate. By increasing the scan rate, we can see the change in the position of the redox peak of the  $CoS_2/CNFs$  composite, which may be due to the occurrence of more sufficient redox reaction during the reaction. There is a linear relationship between the square root of the peak current density and the scanning speed ( $R^2_{anode}=0.99413$ ,  $R^2_{cathode}=0.98439$ ), which indicates that the redox mechanism is limited by the surface reaction.



**Figure 8.** Electrochemical performance of  $CoS_2/CNFs$  (a) CV curves at scan rates ranging from 5 to 40 mV·s<sup>-1</sup>; (b) the relationship between the main redox peak current and the square root of scan rate for the two electrodes; (c) GCD curves of at different current densities from 1 to 10 A·g<sup>-1</sup>; (d)Electrochemical impedance spectra(EIS); (e) CoS<sub>2</sub>/CNFs in specific capacitance retention rates at the current density of 2 A·g<sup>-1</sup> after 2000 cycle.

The reason for the decrease of the linear relationship between the peak current and the square root of the scanning velocity during the discharge process is that the polarization phenomenon occurs under the large sweeping speed. In the constant current charge and discharge diagrams at different current densities (Figure 8c), there is a platform for both charging and discharging, which shows that the energy storage and release process of the  $CoS_2/CNFs$  composite material exhibits redox reaction characteristics.

Table 3 shows the specific capacitance of  $CoS_2/CNFs$  composite material at different current densities. At low current density, the ions diffuse on the surface of the electrode material were sufficient to cause high specific capacitance. At high current density, the time for ion diffusion is limited, which leads to a decrease in specific capacitance. Figure 8d is the ac impedance diagram of the composite material, and the illustration is a magnified view of the high-frequency region. The AC impedance diagram includes a straight line with a semicircle in the high frequency region and a slope in the low frequency region. The X-axis intercept is usually used to represent the solution resistance (Rs) and which consists of the internal resistance of the electrode material and the contact resistance of the electrode/electrolyte interface[45]. In the low frequency region, the slope of the straight line is closer to 90°, indicating that the diffusion rate of ions to the electrode surface is faster[46]. Figure 8e shows the CoS<sub>2</sub>/CNFs cycle characteristics at a current density of 2 A·g<sup>-1</sup> with 2000cyclesofchargeand discharge. That is because the long-term cycle leads to the destruction of electrode materials, resulting in the reduction of redox reaction with the electrolyte, thus resulting in the decrease of specific capacitance.

Sample	$\begin{array}{c} C(F \cdot g^{-1}) \\ 1A \cdot g^{-1} \end{array}$	$\begin{array}{c} C(F \cdot g^{\textbf{-1}}) \\ 2A \cdot g^{\textbf{-1}} \end{array}$	$\begin{array}{c} C(F \cdot g^{-1}) \\ 4A \cdot g^{-1} \end{array}$	C(F·g <sup>-1</sup> ) 6A·g <sup>-1</sup>	$\begin{array}{c} C(F \cdot g^{\text{-}1}) \\ 8A \cdot g^{\text{-}1} \end{array}$	$C(F \cdot g^{-1})$ 10A $\cdot g^{-1}$
CoS <sub>2</sub> /CNFs	380.4	362	346.2	331.3	317.6	308.9

**Table 3.** Specific capacitance of  $CoS_2/CNFs$  (F·g<sup>-1</sup>)

To evaluate the superiority of the prepared electrode materials, Table 4 lists our results compared to previously published of  $CoS_2$  as electrode material.

**Table 4.** The electrochemical data of CoS<sub>2</sub> as electrode material

Cobalt material	<b>Current density</b>	Specific-capacitance	References
CoS <sub>2</sub> /NCNTF	$1.0 \text{ A} \cdot \text{g}^{-1}$	937.0 m Ah $\cdot$ g <sup>-1</sup>	[47]
CoS <sub>2</sub> -N-C/3DGN	$1600 \text{ mA} \cdot \text{g}^{-1}$	$124.0 \text{ mA h} \cdot \text{g}^{-1}$	[48]
CoS <sub>2</sub> –graphene	$0.5 \mathrm{A} \cdot \mathrm{g}^{-1}$	$314.0 \text{ F} \cdot \text{g}^{-1}$	[30]
CoS <sub>2</sub> /CNFs	$1 \text{A} \cdot \text{g}^{-1}$	$380.4.0 \text{ F} \cdot \text{g}^{-1}$	This work

## **4. CONCLUSIONS**

In summary, by using electrospinning and hydrothermal method, the composite material can not only alleviate the agglomeration of cobalt sulfide, but also improved its electrochemical performance.

The cobalt metal ions were added to the carbon nanofibers by electrospinning, and the  $CoS_2$  prepared by hydrothermal method with sulfur source was less likely to fall off from the carbon nanofibers, thus improving the cyclic stability of the cyclic composites. By adjusting the hydrothermal temperature and hydrothermal time, the composite with excellent electrochemical properties was prepared. The composite prepared under the hydrothermal temperature of 150 °C and hydrothermal time of 12 h had the excellent electrochemical performance with a high specific capacitance of 380.4 F·g<sup>-1</sup> at a current density of 1 A·g<sup>-1</sup>. After charging and discharging for 2000 cycles at a current density of 2·A g<sup>-1</sup>, the capacitance retention value was maintained at 90.5%. The remarkable electrochemical properties of  $CoS_2/CNFs$  had indicated that it was a promising electrode material for supercapacitors.

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#### References

- 1. M.J. Zhi, C.C. Xiang, J.T. Li, M. Li and N.Q. Wu, Nanoscale, 5 (2013) 72.
- 2. R. Vinodh, R.S. Babu, C.V.V.M. Gopi, C. Deviprasath, R. Atchudan, L.M. Samyn, A.L.F. de Barros, H. Kim and M. Yi, *J Energy Storage*, 28 (2020) 101196.
- K. Chi, Z.Y Zhang, Q.Y.Lv, C.Y.Xie, J. Xiao, F. Xiao and S. Wang, ACS Appl MaterInterfaces, 9 (2017) 6044.
- 4. B.L. Ellis, P. Knauth and T. Djenizian, Adv. Mater., 45 (2014) 3368.
- 5. A. González, E. Goikolea, J.A. Barrena and R. Mysyk, Renew. Sust. Energ. Rev., 58 (2016) 1189.
- 6. Y.S. Zhou, X.R. Zhou, C. W.Ge, W.Z. Zhou, Y.C. Zhu and B. S. Xu, Mater. Lett., 246 (2019) 174.
- 7. Z.A. Xiao, W.W. Chen, K. Liu, P. Cui, D. Zhan, Int J. Electrochem Sci., 13 (2018) 5370
- 8. G.F. Shi, Z.Wang, C. Liu, G.Y. Wang, S.M. Jia, X. Jiang, Y.C. Dong, Q. Zhang, H.Q. Zhang, X. Li and F.F.Luo, *Int J. Electrochem Sci.*, 14 (2019) 5259.
- 9. H. Chen, Y.C. Guo, F. Wang, G. Wang, P.R. Qi, X. H. Guo, B. Dai and F. Yu, *New Carbon Mater.*, 32 (2017) 592.
- 10. D. Tang, S. Hu, R. Yi, M.L. Gordin, S. Chen, J. Song and D.Wang, ACS Appl MaterInterfaces, 8 (2016) 6779.
- 11. J.H. Yu, F.F. Xie, Z.C. Wu, T. Huang, J.F. Wu, D.D. Yan, C.Q.Huang and L.Li, *Electrochim Acta*, 259 (2018) 968.
- 12. K. Li, J.Q. Liu, Y.S. Huang, F.X. Bu and Y.X. Xu, J Mater Chem A, 5 (2017) 5466.
- 13. J.H. Lu, F. Lian, L.Q. Guan, Y.X. Zhang and F. Ding, J Mater Chem A, 7 (2019) 991.
- 14. H. Huang, S. Gao, A.M. Wu, K. Cheng, X.N. Li, X.X. Guo and J.J Zhao, *Nano Energy*, 31 (2017) 74.
- Z. Wang, C. Liu, G.F. Shi, H. Ma, X. Jiang, Q. Zhang, H.Q. Zhang, Y. Su, J.L. Yu and S.M. Jia, *Ionics*, 25 (2019) 5035.
- 16. Z. Wang, C. Liu, G.F. Shi, G.Y. Wang, H.Q. Zhang, Q. Zhang, X. Jiang, X. Li, F.F. Luo, Y.W. Hu and K.Q. Yi, *Ionics*, 26 (2020) 3051.
- 17. P. Justin and G.R. Rao, Int J Hydrog Energy, 35 (2010) 9709.
- 18. H. Hu, B.Y. Guan and X.W. Lou, Chem-US, 1 (2016) 102.
- 19. Y.H. Zhang, N.N. Wang, C.H. Sun, Z.X. Lu, P. Xue, B. Tang, Z.C. Bai and S.X. Dou, Chem Eng J,

332 (2018) 370.

- 20. J.C. Xing, Y.L. Zhu, Q.W. Zhou, X.D. Zheng and Q.J. Jiao, Electrochim Acta, 136 (2014) 550.
- 21. Q.F. Zhang, C.M. Xu and B.A. Lu, Electrochim Acta, 132 (2014) 180.
- 22. Q.H. Wang, L.F. Jiao, H.M. Du, Y.C. Si, Y.J. Wang and H.T. Yuan, *J Mater Chem.*, 22 (2012) 21387.
- 23. Y.H. Zhang, N.N. Wang, P. Xue, Y.L. Liu, B. Tang, Z.C. Bai and S.X. Dou, *Chem Eng J*, 332 (2018) 370.
- 24. L.L. Feng, M.H. Fan, Y.Y. Wu, Y.P. Liu, G.D. Li, H. Chen, W. Chen, D.J. Wang and X.X. Zou, *J Mater Chem A*, 4 (2016) 6860.
- 25. Z.Y. Wang, L. Zhou, X. Lou and D. Wen, Adv. Mater., 24 (2012) 1903.
- 26. Y.M. Sun, X.L. Hu, J.C. Yu and Q. Li, Energy Environ. Sci., 4 (2011) 2870.
- 27. L. Fei, Q.L. Lin, B. Yuan, G. Chen, P. Xie, Y.L. Li, Y. Xu, S.G. Deng, S. Smirnov and H.M. Luo, ACS Appl. Mater. Interfaces, 5 (2013) 5330.
- 28. M.S. Akhtar, M.A. Khan, M.S. Jeon and O.B. Yang, *Electrochim Acta*, 27 (2008) 7869.
- 29. L. Bao, G. Xu, H. Zeng, L.L. Li, R.Y. Zhao, G. Shen, G.R. Han and S.X. Zhou, *CrystEngComm*, 18 (2016) 2385.
- 30. B. Wang, J. Park, C.Y. Wang, H. Ahn and G.X. Wang, *Journal of Materials Chemistry*, 22 (2012) 15750.
- 31. H.C. Deng, M.W. Zhu, T.X. Jin and Y. Qian, Int J. Electrochem Sci., 15 (2020) 16.
- 32. H. Jie, Y.T. Wang, H.C. Deng, J.F. Chen, J.H. Ding and C.Y. Wang, *Int J. Electrochem Sci.*, 15 (2020) 7272.
- 33. Q.Y. Sun, T.Y. Jiang, G.Z. Zhao and J.Y. Shi, Int J. Electrochem Sci., 14 (2019) 1.
- 34. S. Xie, Y.F. Deng, J. Mei, Z. T. Yang, W.M. Lau and H. Liu, *Electrochim Acta*, 231 (2017) 287.
- 35. J. Xie, S.Y. Liu, G. S. Cao, T.J. Zhu and X.B. Zhao, Nano Energy, 2 (2013) 49.
- 36. H.D. Chul, R. Vinodh, C.M. Gopi, C. Deviprasath, H.J. Kim and M. Yi, *Dalton Trans.*, 48 (2019) 14808.
- 37. S. Dou, L. Tao, J. Huo, S.Y. Wang and L.M. Dai, EnergyEnviron Sci., 4 (2016) 1320.
- 38. Y. Ji, X.Y. Liu, W. Liu, Y. Wang, H.D. Zhang, M. Yang, X.F. Wang, X.D. Zhao and S.H. Feng, RSC Adv, 4 (2014) 50220.
- 39. B. Wang, J. Park, D. Su, C.Y. Wang, H. Ann and G.X. Wang, J Mater Chem 22 (2012) 15750.
- 40. J.W. Xiao, L. Wan, S.H. Yang, F. Xiao and S. Wang, Nano Lett, 14 (2014) 831.
- 41. S. Vemskateshalu, D. Rangappa and A. N. Grace, Int. J. Nanosci., 16 (2017) 1760020.
- 42. R. Ren, M.S. Faber, R. Dziedic, Z.H. Wen, S. Jin, S. Mao and J.H. Chen, *Nanotechnology*, 26 (2015) 494001.
- 43. S.Y. Zhai, L.L. Lei and M.G. Wang, Ionics, 23 (2017) 1.
- 44. M.L. Mao, L. Mei, L.C. Wu, Q.H. Li and Z. Ming, RSC Adv., 4 (2014) 12050.
- 45. Z. Wang, C. Liu, G.F. Shi, G.Y. Wang, Q. Zhang, H.Q. Zhang, Y. Su, Y.J. Lei, X. Li, F.F. Luo, Y.W. Hu and K.Q. Yi, *Ionics*, 26 (2020) 5737.
- 46. A.S. Justin, P. Vickraman and B.J. Reddy, Curr Appl Phys., 3 (2019) 295.
- 47. C. Chen, M.K. Wu, K.T ao, J.J. Zhou, Y.L. Li, X. Han and L. Han Dalton Trans., 47 (2018) 5639.
- 48. J.T. Zhang, L. Yu and X.W. Lou, Nano Res, 10 (2017) 4298.
- 49. J.B. Song, C.Y. Zhang, J.H. Zhang, H. Zhou, L.Chen, L.L. Bian and A.H. Yuan, J Nanopart Res., 5 (2019) 89.

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