

Article

Preparation and Capacitive Properties of Ni-Doped Zinc Cobaltate/Carbon Fiber Composite Porous Mesh Materials

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Abstract: Nickel-element-doped zinc cobaltate/carbon fiber composites (Ni-ZnCo₂O₄/CF) were prepared on carbon cloth (made of a combination of carbon fibers) conductive substrates using a simple ambient stirring method combined with heat treatment. Characterization tests of the materials revealed that the prepared products were porous Ni-ZnCo₂O₄/CF mesh structures. This porous network structure increases the surface area of the material and helps shorten the diffusion path of ions and electrons. The samples were analyzed using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) methods to investigate the effect of Ni elemental doping on the stability of the materials. The results show that there are no other impurity peaks and no other impurity elements in the Ni-ZnCo₂O₄/CF electrode material, which indicates that the sample purity is high. Meanwhile, the electrochemical properties of Ni-ZnCo₂O₄/CF electrode materials were studied. Under the condition of 15 A·g⁻¹, the specific capacitance of Ni-ZnCo₂O₄/CF electrode material is 1470 F·g⁻¹, and after 100 cycles, its specific capacity reaches 1456 F·g⁻¹, which is 99.0% of the specific capacity of 1470 F·g⁻¹, indicating that the electrode material has good stability. In addition, we assembled asymmetric supercapacitors (Ni-ZnCo₂O₄/CF // CNTs) with Ni-ZnCo₂O₄/CF as the positive material and carbon nanotubes (CNTs) as the negative material. In the cyclic stability experiment of Ni-ZnCo₂O₄/CF/CNTs devices, when the current density was 1 A·g⁻¹, the specific capacitance was 182 F·g⁻¹. After 10,000 cyclic charge–discharge tests, the specific capacity became 167 F·g⁻¹, which was basically unchanged compared with the initial specific capacity, reaching 91.8%. It shows that it has higher charge–discharge performance and higher cycle stability.

Keywords: zinc cobaltate; electrodes; mixing method at room temperature; composite material; ultra-capacitor



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1. Introduction

At the same time as rapid industrial development, problems such as environmental pollution and energy supply shortage have caused great inconvenience to people's production and life [1]. Electricity is an economical, practical, clean, easy-to-control and -convert energy, which is suitable for a variety of environments. However, electricity has the fatal disadvantage of being difficult to store. In order to realize the effective storage and use of energy, it is necessary to design an energy storage device with high efficiency and high stability [2]. Supercapacitors have the advantages of long service life, high power density, fast charging speed, and environmental protection [3]. At the same time, water pollution is also a major environmental problem currently being faced; rational use of light energy to achieve efficient degradation of organic matter in water can not only solve the energy crisis but can also effectively protect the environment. Therefore, there is an urgent need to develop new photocatalytic materials with good electrochemical properties and high efficiency. The microstructure of the material has an important effect on its electrochemical performance and catalytic activity [4,5].

Bimetallic oxide materials have high electrical conductivity, high theoretical specific capacity, good oxidation–reduction reversibility and high specific capacity [6,7]. Among them, zinc cobaltate (ZnCo_2O_4) is considered to be a potential supercapacitor electrode material because of its excellent electrochemical performance, high conductivity, low price, and green environmental protection characteristics, but its specific capacity and energy storage performance still need to be improved. By doping Ni elements, not only can this process improve its specific capacity, but it can also effectively store electrical energy and will not reduce its service life and conductivity.

In this paper, nickel-doped zinc cobaltate composites ($\text{Ni-ZnCo}_2\text{O}_4/\text{CF}$) with a porous network structure were synthesized on carbon cloth (made of a combination of carbon fibers) by the room-temperature stirring method combined with heat treatment. These materials have abundant pore structures, which are favorable for the transport of ions and electrons in the electrolyte. The results show that the synthesized cobalt cobaltate has a homogeneous network structure without other impurity peaks and high purity. The specific capacitance of $\text{Ni-ZnCo}_2\text{O}_4/\text{CF}$ was $1470 \text{ F}\cdot\text{g}^{-1}$ at a current density of $15 \text{ A}\cdot\text{g}^{-1}$ and was 99.0% of the initial specific capacity after 100 changes. The prepared $\text{Ni-ZnCo}_2\text{O}_4/\text{CF}$ materials were also assembled into asymmetric supercapacitor devices ($\text{Ni-ZnCo}_2\text{O}_4/\text{CF} // \text{CNTs}$) by using the prepared $\text{Ni-ZnCo}_2\text{O}_4/\text{CF}$ materials as the anode materials and carbon nanotubes (CNTs) as the anode materials. The specific capacity of $\text{Ni-ZnCo}_2\text{O}_4/\text{CF} // \text{CNTs}$ reaches $182 \text{ F}\cdot\text{g}^{-1}$ at a current density of $1 \text{ A}\cdot\text{g}^{-1}$, and after 10,000 charge/discharge tests, its specific capacity becomes 91.8% of the original one, which shows that the prepared material has good cycling performance and good cycle stability during the charging and discharging process.

2. Materials and Methods

2.1. Instruments

In this experiment, a scanning electron microscope (SEM, model S4800, acceleration voltage 0.1~30 kv, magnification $20\times\sim 800,000\times$) and a transmission electron microscope (TEM, JEM-2100F) were used to observe the micro-morphology of the samples. The phase structure of the prepared materials was analyzed by X-ray diffractometer (XRD, XRD-700). The components of the prepared samples were analyzed by X-ray energy-dispersive spectrometry (EDS, JEM-2100Plus), a multi-channel workstation (1470E CellTest), and an electrochemical impedance test system (LEIS370/470). The samples required for experimental preparation are shown in Table 1.

Table 1. List of raw materials used in these experiments.

Drug Names	Molecular Formula	Manufacturer
Zinc Nitrate Hexahydrate	$\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$	Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China)
Cobaltous nitrate hexahydrate	$\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$	Tianjin Hiens Opdex Technology Co., Ltd. (Tianjin, China)
Ammonium fluoride	NH_4F	Langfang Qian Yao Chemical Reagent Co., Ltd. (Langfang, China)
Urea	$\text{CH}_4\text{N}_2\text{O}$	Anhui Haoyuan Chemical Group Co., Ltd. (Fuyang, China)
Carbon cloth	C	Jiangsu Sutong Carbon Fiber Co., Ltd. (Nantong, China)
carbon nanotube	C	Jiangsu Cnano Technology Co., Ltd. (Zhenjiang, China)
Nickel nitrate hexahydrate	$\text{Ni}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$	Nanjing Chemical Reagent Co., Ltd. (Nanjing, China)

2.2. Preparation of ZnCo_2O_4

Firstly, 3.5 mmol of $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ was dissolved in 45 mL of deionized water. Then, 2 mmol of $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, 2 mmol of NH_4F , and 4 mmol of urea were gradually added into the solution. At the same time, 1 cm^2 of carbon cloth (carbon fiber combination) conductive substrate was added. Use a magnetic stirrer to stir for 5 h, remove and prepare the sample, and then wash it repeatedly with anhydrous ethanol and deionized water. The precursor $\text{ZnCo}_2\text{O}_4/\text{CF}$ was obtained by transferring the cleaned sample to the oven for drying at 50°C for 5 h. Finally, $\text{ZnCo}_2\text{O}_4/\text{CF}$ electrode materials were obtained by placing

ZnCo₂O₄/CF precursor in a Muffle furnace and heating at room temperature to 400 °C for 2 h.

2.3. Preparation of Ni-ZnCo₂O₄/CF Materials

The ZnCo₂O₄/CF material obtained above was dissolved in 45 mL of deionized water, and the Ni(NO₃)₂·6H₂O solution was added to the solution drop by drop, stirring for 3 h with a magnetic agitator, taking out the sample for preparation, and then washing repeatedly with anhydrous ethanol and deionized water. The precursor of Ni-ZnCo₂O₄/CF was obtained by transferring the cleaned sample to the oven for drying at 50 °C for 4 h. Finally, Ni-ZnCo₂O₄/CF electrode material was obtained by placing the precursor in a Muffle furnace at room temperature to 400 °C for 2 h. The preparation of porous Ni-ZnCo₂O₄/CF in the experiment is shown in Figure 1.

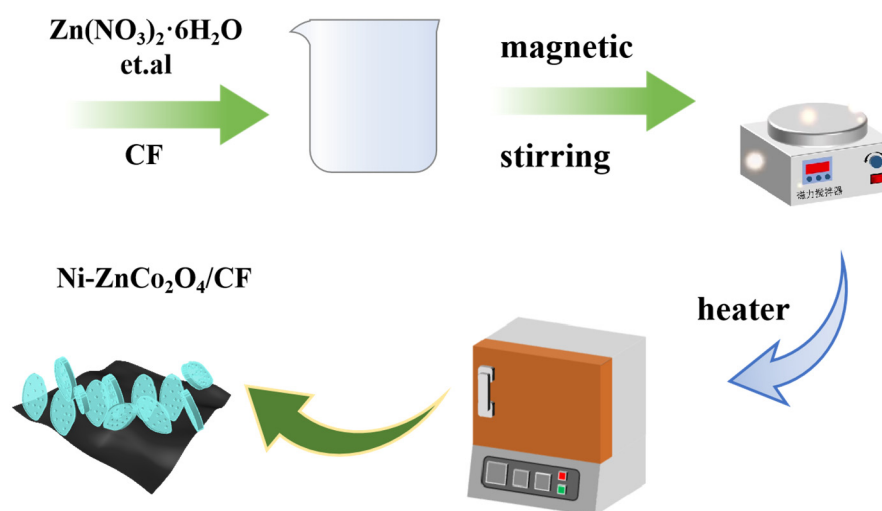


Figure 1. Schematic diagram of the preparation process of porous Ni-ZnCo₂O₄/CF material.

2.4. Nitrogen Adsorption and Desorption Test

A 500 mg amount of the sample to be tested was loaded into the sample tube, and the sample tube was loaded into the degassing station. Then, put the heating pack on the sample tube, turn on the vacuum pump, and start to evacuate the sample for 30 min. Next, turn on the heating switch and heat it for 5 h in order to remove the gas adsorbed on the surface of the material. After the degassing was finished, the heating power was turned off and the sample was cooled to room temperature and then backfilled with helium. After filling the sample with helium at atmospheric pressure, the sample tube was removed and immediately capped with a rubber stopper, weighed, and recorded. Load the weighed tubes into the analyzer station. Liquid nitrogen is added to the Dewar's flask, and the calculated sample mass is entered into the analytical file to begin adsorption and desorption testing.

2.5. Assembly of Asymmetric Supercapacitors

Assembly of asymmetric electrochemical capacitors: Porous Ni-ZnCo₂O₄/CF/CNTs asymmetric devices were prepared by using porous Ni-ZnCo₂O₄/CF composite material as the positive electrode, carbon nanotubes (CNTs) as the negative electrode, KOH as the electrolyte, and a diaphragm between the positive and negative electrodes. The relevant calculation formulas are as follows:

$$C_s = i\Delta t / m\Delta V \quad (1)$$

$$E = 0.5C_s\Delta V^2 \quad (2)$$

$$P = 3600E / \Delta t \quad (3)$$

$$q = C_S \Delta V m \quad (4)$$

$$m^+ / m^- = C^- \Delta V^- / C^+ \Delta V^+ \quad (5)$$

where: C_S (specific capacity, $F \cdot g^{-1}$); Δt (discharge time, s); m (mass of active material, g); E (Energy density, $W \cdot h \cdot kg^{-1}$); P (Power density, $W \cdot kg^{-1}$).

3. Results and Discussion

Figure 2a,b are SEM images of Ni-ZnCo₂O₄/CF materials at different magnifications. It was observed by scanning electron microscope that the Ni-ZnCo₂O₄/CF composites prepared by stirring at room temperature were arranged and distributed in a network. As shown in Figure 2c–f, the prepared material contains the elements Zn, Co, O, and Ni. Experiments show that there are no other impurities in the synthesized products. The similar distribution of elemental Zn and O may indicate specific interactions between them, possibly chemical reactions or physical adsorption. The different distributions observed for the elements Co and Ni may imply that they may have undergone different chemical reaction paths in the samples. This may be due to their different chemical properties or influenced by the sample treatment conditions.

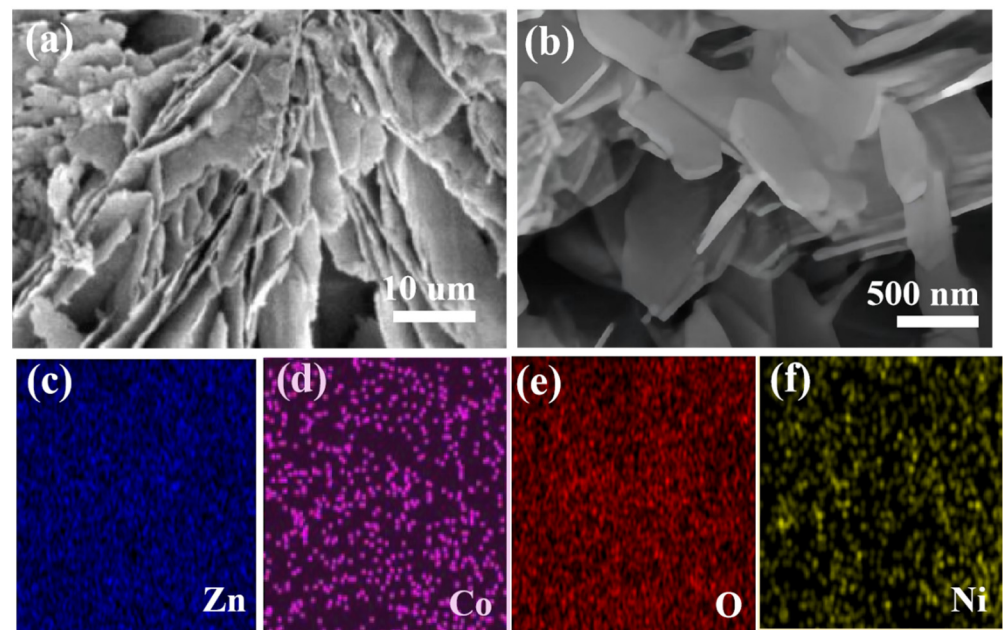


Figure 2. SEM images of (a,b) Ni-ZnCo₂O₄/CF materials at different magnifications; (c–f) mapping of Ni-ZnCo₂O₄/CF materials.

In order to better observe the microstructure of Ni-ZnCo₂O₄/CF composites, the microstructure was characterized by transmission electron microscopy. The result is shown in Figure 3. From the inner region of Figure 3a, a clear nanosheet-like structure is visible, and these nanosheets are stacked on top of each other to form pores, which is also consistent with the phenomenon observed in Figure 2. As can be seen from the HRTEM diagram in Figure 3b, the crystal plane spacing of the lattice fringes is 0.23 nm and 0.24 nm, corresponding to the (222) and (311) lattice planes of Ni-ZnCo₂O₄/CF, respectively. It was found that there are good diffraction rings in the obtained products, indicating that the compounds are polycrystalline.

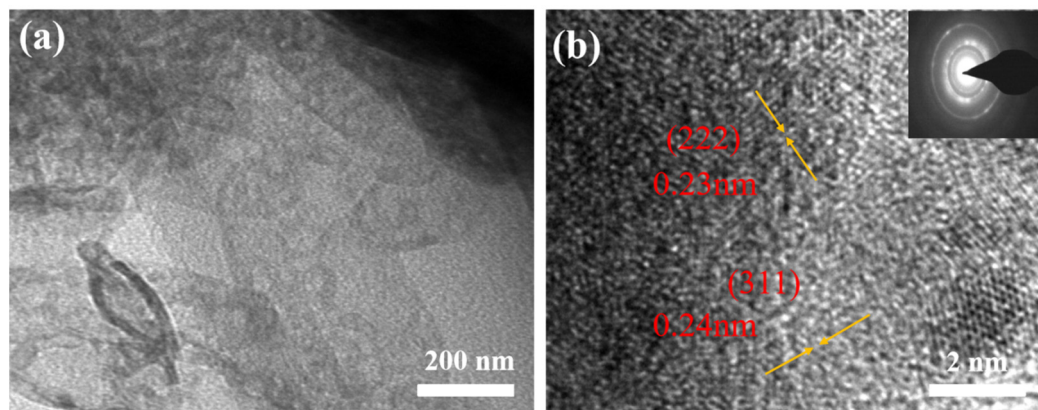


Figure 3. (a) TEM image of porous Ni-ZnCo₂O₄/CF nanomaterials; (b) HRTEM image of porous Ni-ZnCo₂O₄/CF nanomaterials.

Figure 4a presents the X-ray diffraction (XRD) analysis of the Ni-ZnCo₂O₄/CF composite. The illustration reveals the crystallographic makeup of the Ni-ZnCo₂O₄/CF material captured via sharply defined and singular diffraction peaks, signifying a high level of crystallization and superior product purity within the prepared sample. These discernible diffraction lineages align well with the cubic ZnCo₂O₄ spinel structure (JCPDF: 01-1149). Peaks occurring at 2-theta values of 19.06°, 31.48°, 36.96°, 38.8°, 45.04°, 55.66°, 59.76°, and 65.36° correspond to the (111), (220), (311), (222), (400), (422), (511), and (440) crystal facets, respectively [8]. Figure 4b offers an exposition of the Energy-Dispersive Spectroscopy (EDS) findings pertaining to the porous Ni-ZnCo₂O₄/CF network structure. The data confirm that the structure exclusively comprises Zn, Co, O, and Ni constituents, thereby validating the absence of detrimental impurity elements. The convergence of these outcomes empirically proves the successful doping of Ni element.

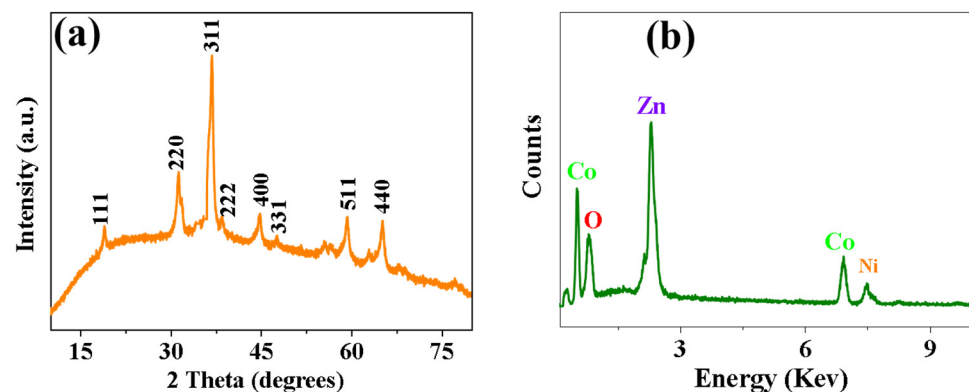


Figure 4. (a) XRD patterns of porous Ni-ZnCo₂O₄/CF nanomaterials; (b) EDS spectra of porous Ni-ZnCo₂O₄/CF nanomaterials.

Figure 5a unveils the cyclic voltammetric curves of the carbon cloth conductive substrate, ZnCo₂O₄, and Ni-ZnCo₂O₄/CF, sweeping at a rate of 10 mV·s^{−1}. The confined region by the voltammetry curve for the carbon cloth substrate is notably compact, implying that its specific capacity within the electrochemical reaction procedure is modest and virtually inconsequential. Contrarily, the area encapsulated by the curve for Ni-ZnCo₂O₄/CF material is impressively expansive, highlighting a significant enhancement in both the specific capacity and charge storage aptitude following the incorporation of Ni elements. Figure 5b delineates the cyclic voltammetry curves of the porous Ni-ZnCo₂O₄/CF mesh recorded at scan rates of 5, 10, 30, and 50 mV·s^{−1}, within the potential window of −0.2~0.6 V. The figure exhibits that as the scan rate experiences an amplification, there is a proportionate surge in the area cordoned off by the cyclic voltammetric curves, an

indication of an adept charge transfer for the material under investigation. Characteristic oxidation peaks are prominently noticeable nearing the potential window of 0.4 V. At the same time, the emergence of discernible reduction peaks can be observed at the potential window of 0.2 V. These shreds of evidence collectively suggest the occurrence of a redox reaction in the Ni-ZnCo₂O₄/CF electrode material, signaling a distinctive pseudocapacitive charge–discharge storage mechanism.

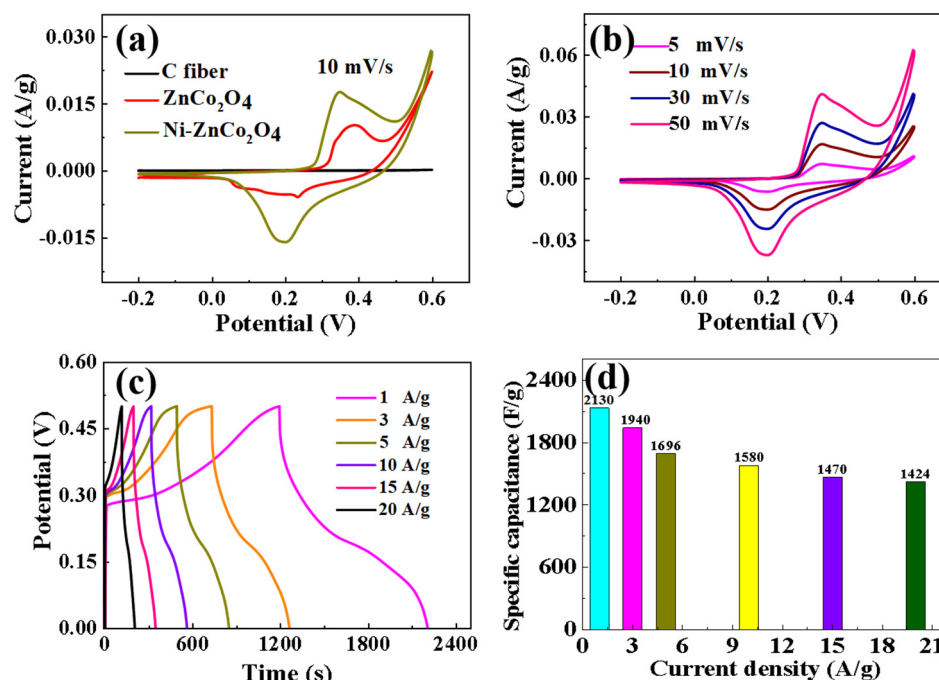


Figure 5. (a) Showcases the CV curves of carbon fiber, ZnCo₂O₄, and Ni-ZnCo₂O₄/CF, conducted at a scanning speed of 10 mV·s^{−1}. (b) Illustrates the CV curves of Ni-ZnCo₂O₄/CF composites at varying scanning speeds of 5, 10, 30, and 50 mV·s^{−1}. (c) Presents the charge/discharge diagrams of Ni-ZnCo₂O₄/CF composites at assorted current densities. (d) Depicts the specific capacitance diagram of Ni-ZnCo₂O₄/CF composites across multiple current densities.

Figure 5c shows the charging and discharging test results of the Ni-ZnCo₂O₄/CF material at different current densities. Experiments show that the material has good electrochemical performance during the charge–discharge process, its charge–discharge curve is basically symmetric, and the specific capacitance of the Ni-ZnCo₂O₄/CF material is calculated based on the charge–discharge curve of the material, as shown in Figure 5d, and the porous Ni-ZnCo₂O₄/CF electrode material at the current densities of 1, 3, 5, 10, 15, and 20 A·g^{−1}. The specific capacitances were 2130, 1940, 1696, 1580, 1470, and 1424 F·g^{−1}, respectively. The electrochemical properties of Ni-ZnCo₂O₄ nanomaterials and comparison with references [9–12] are given in Table 2.

Specific surface area and pore size have an important influence on the performance of the material, and we further carried out relevant tests on the material, as shown in Figure 6. Figure 6a,b show the specific surface area curves and pore size distribution curves of ZnCo₂O₄ material with the values of 99.02 m²/g and near 30 nm, respectively, and Figure 6c,d show the specific surface area curves and pore size distribution curves of Ni-ZnCo₂O₄ material with the values of 109.31 m²/g and near 32 nm, respectively. Comparison reveals that the Ni-ZnCo₂O₄ material has a larger specific surface area and a richer pore structure. This property enables the electrolyte and electrode materials to come into contact more fully, provides more electrochemical reaction sites, and shortens the electron and ion transport distance, thus increasing the reaction rate and helping to enhance the electrochemical performance of the materials.

Table 2. Comparative Analysis of the Properties of the Electrode Materials Presented in this Study and those Documented in the Literature.

Electrode Material	Current Density/(A/g)	Specific Capacitance/(F/g)	Cycle Number	Capacitance Retention/%	Ref.
Hollow cotton carbon-based NiCo ₂ S ₄ /NiMoO ₄ hybrid arrays	5.0	2323	10,000	90.0	[9]
OV-ZnCo ₂ O ₄	1.0	211.6			[10]
NiMoO ₄ /CoMoO ₄ nanorods	1.0	1445	3000	78.8	[11]
ZnCo ₂ O ₄ @NiCo ₂ O ₄	1.0	1728.1	10,000	91.3	[12]
Ni-ZnCo ₂ O ₄	1.0	2130	10,000	91.8	This paper

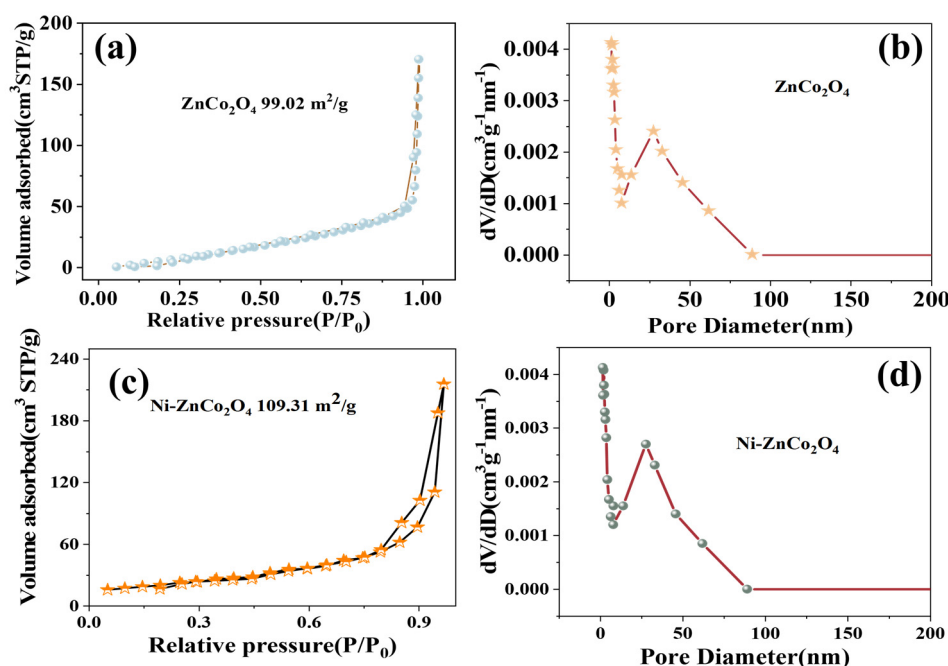


Figure 6. Presents the N₂ adsorption/desorption plots and pore size distribution analyses for both ZnCo₂O₄ and Ni-ZnCo₂O₄. Specifically, parts (a,b) exhibit the N₂ adsorption/desorption trajectories and corresponding pore size dispersal patterns for ZnCo₂O₄, respectively. Parts (c,d), on the other hand, depict the N₂ adsorption/desorption curves and pore size distribution profiles for the Ni-ZnCo₂O₄ composite.

Figure 7a shows the impedance curves of ZnCo₂O₄/CF material and Ni-ZnCo₂O₄/CF material. The curves in the figure consist of high and low frequencies, with the high-frequency region representing the impedance of the ions passing through the surface film of the electrode material and the low-frequency region representing the charge-transfer impedance. In general, the value of the horizontal axis indicates R_s, and its value can be read according to the intercept of the curve and the horizontal axis; it can be seen that the intercept of the Ni-ZnCo₂O₄/CF material is smaller than that of the ZnCo₂O₄/CF material, which proves that the Ni-ZnCo₂O₄/CF material has good electrical conductivity. The diameter of the curve similar to a semicircle in the high-frequency region is denoted as R_{ct}, and the value of R_{ct} is correlated with the semicircle diameter; it can be seen in the figure that the radius of the Ni-ZnCo₂O₄/CF material is smaller than that of the ZnCo₂O₄/CF material, indicating that the Ni-ZnCo₂O₄/CF has a good charge-transferring ability. Figure 7b illustrates the cyclic stabilization properties of the material at different current densities after repeating 100 cycles. As shown, at a current density of 15 A·g⁻¹,

the material has a specific capacitance of $1470 \text{ F}\cdot\text{g}^{-1}$. After every 100 changes, the current density was restored to $15 \text{ A}\cdot\text{g}^{-1}$, and its specific capacitance was $1456 \text{ F}\cdot\text{g}^{-1}$, which was 99.0% of the original specific capacitance. The results show excellent multiplicity performance and cycling stability at different current densities, and the decrease in the specific capacity of the materials is very small, which is due to the fact that a few materials cannot fully participate in the reaction, and a few irreversible changes during the process of current increase.

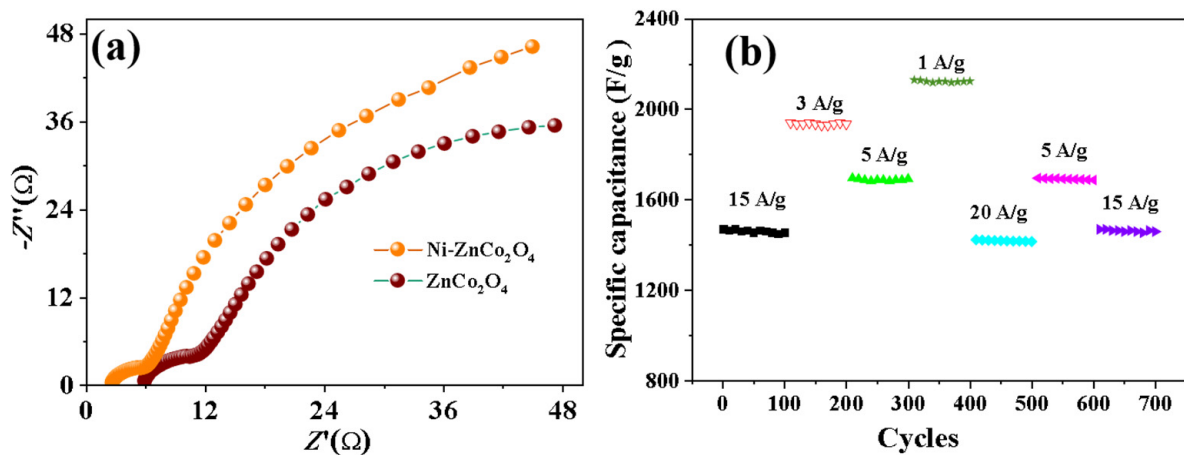


Figure 7. (a) Nyquist plots of Ni-ZnCo₂O₄/CF composites versus ZnCo₂O₄/CF materials; (b) rate and cycling performance of Ni-ZnCo₂O₄/CF composites at different current densities.

In order to further study the practical application value of Ni-ZnCo₂O₄/CF composites, we assembled Ni-ZnCo₂O₄/CF composites // CNTs asymmetric supercapacitors. The Ni-ZnCo₂O₄/CF composite is the positive electrode, and the CNTs are the negative electrode, because the carbon nanotubes have a very high specific surface area, which means that more surface area is available for charge storage per unit mass or per unit volume, and they have excellent electrical conductivity, which enables them to transport electrons quickly, thus reducing the charge transport impedance and improving the charge and discharge speeds and performance of the supercapacitor [13,14]. A schematic diagram of the supercapacitor structure is shown in Figure 8.

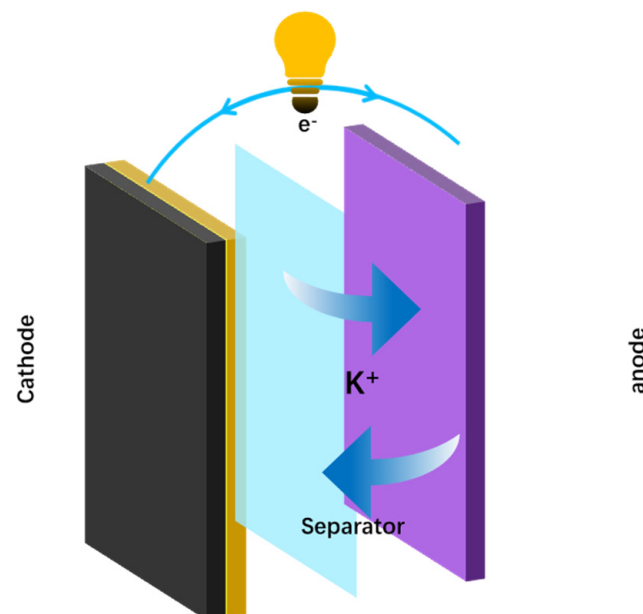


Figure 8. Schematic diagram of the working principle of the supercapacitor device.

First, the experiment was conducted to test the negative electrode material to explore the electrochemical performance of this material under different currents, as shown in Figure 9. Figure 9 shows the charging/discharging curves of CNTs electrodes at different current densities. The constant-current charging and discharging curves are triangularly symmetric, indicating good reversibility of charging and discharging. The specific capacities of the CNTs electrodes were calculated as 262, 238, 218, 184, 162, and 152 $\text{F}\cdot\text{g}^{-1}$ based on the discharge curves at current densities of 1, 3, 5, 10, 15, and 20 $\text{A}\cdot\text{g}^{-1}$, respectively.

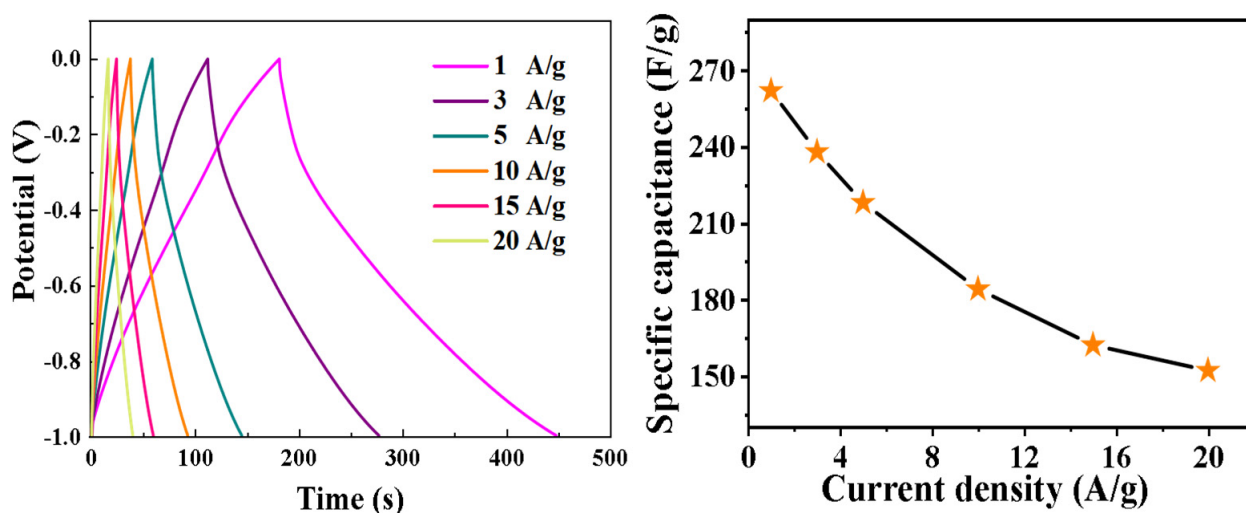


Figure 9. Charge/discharge curves of carbon nanotube electrodes at different current densities and corresponding specific capacities.

Figure 10a unfolds the comparative CV curves for the electrode materials of carbon nanotubes (CNTs) and nickel-zinc cobaltate ($\text{Ni-ZnCo}_2\text{O}_4/\text{CF}$). The $\text{Ni-ZnCo}_2\text{O}_4/\text{CF} // \text{CNTs}$ asymmetric supercapacitor device was constructed utilizing $\text{Ni-ZnCo}_2\text{O}_4$ and carbon nanotubes as electrode materials. Specifying $\text{Ni-ZnCo}_2\text{O}_4/\text{CF}$ as the positive electrode and carbon nanotubes as the negative electrode, the disparity amidst the positive and negative potential windows was employed as the voltage span. Upon computation, a theoretical potential window of 1.6 V was derived. Figure 10b portrays the cyclic voltammetry curves subsisting under varying voltage windows. These curves maintain a roughly congruous form across different voltage windows, confirming the commendable reversibility of the device. Figure 10c delineates the CV plot for the $\text{Ni-ZnCo}_2\text{O}_4/\text{CF} // \text{CNTs}$ apparatus at assorted scan rates, within the voltage window range of 0–1.6 V. Conversely, Figure 10d showcases the CV profile of the identical device. As the scanning rate escalates, the area within the curve witnesses an enlargement, albeit the general form remains inherently stable, indicating impressive steadiness. Figure 10d also highlights the charge–discharge plots for the $\text{Ni-ZnCo}_2\text{O}_4/\text{CF} // \text{CNTs}$ at fluctuating current densities, with the results manifesting commendable electrochemical reversibility of the material. As depicted in Figure 10e, cycle stability tests were conducted on the $\text{Ni-ZnCo}_2\text{O}_4/\text{CF} // \text{CNTs}$ devices, where the specific capacitance attenuated from the initial $182 \text{ F}\cdot\text{g}^{-1}$ to $167 \text{ F}\cdot\text{g}^{-1}$ following 10,000 testing cycles at a current density of $1 \text{ A}\cdot\text{g}^{-1}$, yielding a cycle stability of 91.8%. The experimental outcomes thereby substantiate the admirable cycle stability and longevity of the electrode material. Lastly, Figure 10f compares the energy density and power density of the device against other energy storage devices [12,15–17]. This device stands out, with a paramount energy density of 73.4 Wh/kg and a power density of 923 W/kg . This competitive edge makes the device fabricated in this research significantly superior to its peers in the field, as referred to in the pertinent literature.

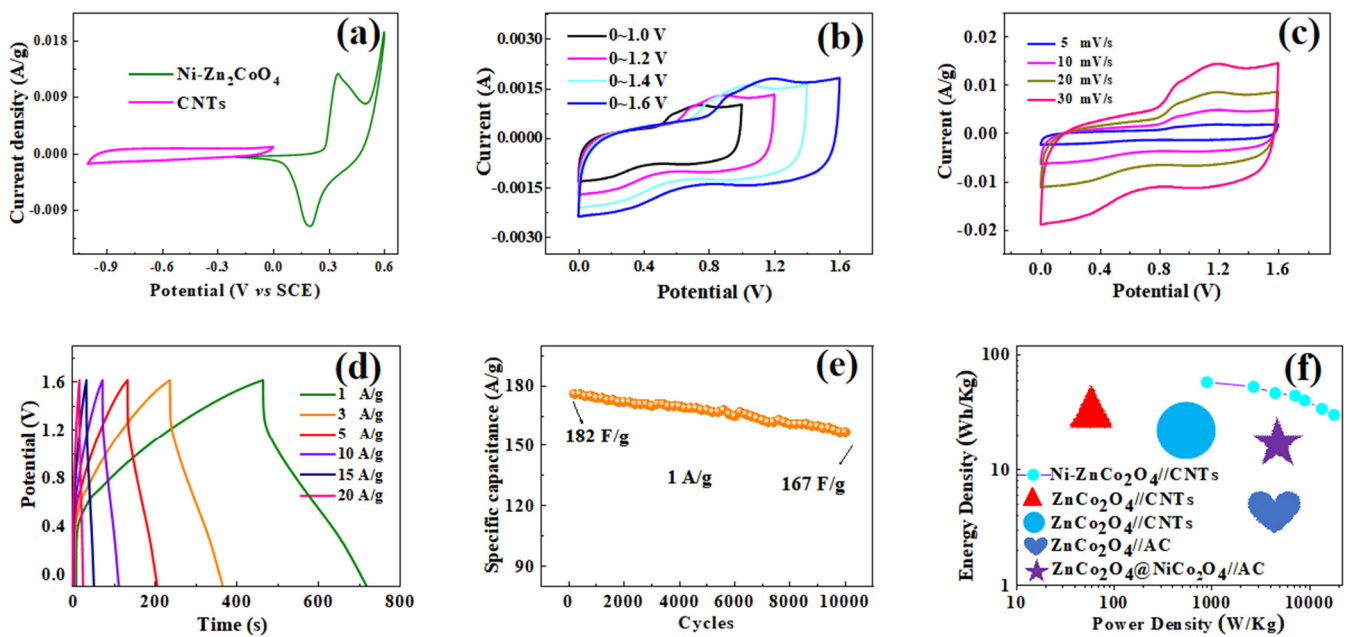


Figure 10. (a) CV curves of Ni-ZnCo₂O₄/CF and CNTs electrodes; (b) CV curves of Ni-ZnCo₂O₄/CF//CNTs devices at different potential windows; (c) CV profiles of Ni-ZnCo₂O₄/CF//CNTs devices at different scan rates; (d) Charge and discharge curves of Ni-ZnCo₂O₄/CF//CNTs devices at different current densities; (e) Performance of Ni-ZnCo₂O₄/CF//CNTs devices at 10,000 cycles at 1 A·g⁻¹ current density; (f) Comparison between Ni-ZnCo₂O₄/CF//CNTs devices and other devices (See Refs. [12,15–17]).

4. Conclusions

In this paper, nickel-element-doped zinc cobaltate/carbon fiber composites were prepared on a carbon cloth substrate composed of carbon fibers by using a simple room-temperature stirring method combined with heat treatment, and the samples have the advantages of porous network structure, high purity, and high cycling performance. The electrochemical properties of the Ni-ZnCo₂O₄/CF electrode materials were investigated. The electrode has a specific capacitance of 1470 F·g⁻¹ at a current density of 15 A·g⁻¹ and is able to maintain a specific capacity of 99.0% for every 100 changes in current density. The Ni-ZnCo₂O₄/CF//CNTs device was subjected to 10,000 charge/discharge tests at a current density of 1 A·g⁻¹, and its specific capacity stability reached 91.8%. The above experiments proved that the electrode material exhibited better cycle stability and cycle life during the charge–discharge process.

Author Contributions: D.C., Y.L., J.W. (Jun Wang) and T.M. carried out the experiments and wrote the manuscript, and J.W. (Jing Wang) designed this experiment and wrote the manuscript and other analyses. H.Z., W.X. and Y.W. carried out the characterization tests, analyzed, and wrote the results. All authors have read and agreed to the published version of the manuscript.

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