

Article

Morphology Modulation of ZnMn_2O_4 Nanoparticles Deposited In Situ on Carbon Cloth for Supercapacitors

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Abstract: As a typical spinel structure material, ZnMn_2O_4 has been widely researched in the field of electrode materials. However, ZnMn_2O_4 nanoparticles as electrode materials for supercapacitors have the disadvantages of low conductivity, inferior structural integrity, and easy aggregation, resulting in unsatisfying electrochemical performance. In this work, we use a hydrothermal method and high-temperature calcination to deposit ZnMn_2O_4 nanoparticles on carbon cloth and explore the influence of hydrothermal reaction time on the deposition morphology and distribution of ZnMn_2O_4 nanoparticles on carbon cloth. The deposition process of ZnMn_2O_4 nanoparticles on carbon cloth was analyzed, and a ZMO-9 electrode was deduced to be the most suitable electrode for supercapacitors. A series of electrochemical performance tests show that the ZMO-9 electrode has excellent specific capacitance (specific capacity) ($499 \text{ F}\cdot\text{g}^{-1}$ ($299.4 \text{ C}\cdot\text{g}^{-1}$) at a current density of $1 \text{ A}\cdot\text{g}^{-1}$) and rate performance (75% capacitance retention at a current density of $12 \text{ A}\cdot\text{g}^{-1}$). The assembled asymmetric supercapacitor has an energy density of $46.6 \text{ Wh}\cdot\text{kg}^{-1}$ when the power density is $800.1 \text{ W}\cdot\text{kg}^{-1}$. This work provides a reference for the structural design of ZnMn_2O_4 supercapacitor electrode materials and the improvement of electrochemical properties.

Keywords: morphology modulation; hydrothermal reaction time; ZnMn_2O_4 ; electrochemical performance; supercapacitor



Citation: Li, C.; Feng, X.; Zhou, J.; Zhao, G.; Cheng, K.; Yu, H.; Li, H.; Yang, H.; Zhao, D.; Wang, X. Morphology Modulation of ZnMn_2O_4 Nanoparticles Deposited In Situ on Carbon Cloth for Supercapacitors. *Metals* **2024**, *14*, 841. <https://doi.org/10.3390/met14080841>

Academic Editor: Henrik K Hansen

Received: 20 June 2024

Revised: 11 July 2024

Accepted: 19 July 2024

Published: 23 July 2024



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1. Introduction

As an important research direction in the field of energy storage, supercapacitors have been widely studied by researchers [1]. The composition and structure of cathode materials determine the electrochemical performance of supercapacitors. Carbon materials, as typical supercapacitor electrode materials, have the advantages of high specific surface area, outstanding conductivity, and excellent chemical stability [2]. But the disappointing specific capacitance of carbon materials limits their further application in supercapacitors. Transition metal oxides, as typical supercapacitor electrode materials, can contact electrolyte ions and cause multiplicity redox reactions in electrochemical reaction processes, which can result in multiple electron transfers and increase the specific capacitance of electrode material effectively [3]. However, the collapse of the structure, high resistance, and easy aggregation of materials during the long cycle lead to problems in the use of transition metal oxides (TMOs) as positive electrode materials for supercapacitors [4]. Therefore, researchers have tried to combine carbon materials with TMOs to achieve the advantages of the above materials [5–8].

Among carbon materials, carbon cloth possesses unique ductility and flexibility as a conductive textile [9]. Therefore, carbon cloth has received a lot of research attention in wearable applications. The direct deposition of TMOs on carbon cloth can prevent the agglomeration of TMOs and avoid the participation of binders, achieving excellent specific

capacitance for supercapacitor electrode materials [10–12]. As one of the most popular materials in the field of energy research, ZnMn_2O_4 with a unique AB_2O_4 spinel structure has high theoretical specific capacitance, low potential, abundant natural reserves, and multiple oxidation valence states of manganese [13,14]. Based on the above advantages, ZnMn_2O_4 is considered one of the most promising TMOs in the field of electrode materials. However, the application of ZnMn_2O_4 as an electrode material has been more focused on lithium-ion batteries [15–17]. In the process of charge and discharge cycles of lithium batteries, the ZnMn_2O_4 electrode has low conductivity, serious volume expansion, easy powdering, and other problems [18], which limit its further development and application in the field of batteries. At the same time, there are few studies on ZnMn_2O_4 as an electrode material for supercapacitors, and these studies have focused on the preparation of ZnMn_2O_4 nanoparticles. The electrochemical performance of ZnMn_2O_4 electrode materials can be improved by adjusting the structure of ZnMn_2O_4 nanoparticles [19]. However, the methods for improving the electrochemical performance of supercapacitor electrode materials by regulating the structure of ZnMn_2O_4 nanoparticles are seldom studied deeply.

Based on the above discussion, it is of great reference significance to expand the application of ZnMn_2O_4 in the field of energy storage to study the regulation method of ZnMn_2O_4 nanostructures used to improve their electrochemical performance as supercapacitor electrode materials. Therefore, a series of ZnMn_2O_4 nanoparticles are deposited on carbon cloth using a hydrothermal method and high-temperature calcination in this work. The deposition process of ZnMn_2O_4 nanoparticles on carbon cloth and the formation mechanism of shuttle-like ZMO-9 nanoparticles are studied by analyzing the morphology and distribution of ZnMn_2O_4 nanoparticles under different hydrothermal reaction times. The electrochemical performance of the ZnMn_2O_4 electrode materials is tested, and the ZMO-9 electrode has the best electrochemical performance, including specific capacitance (specific capacity) ($499 \text{ F} \cdot \text{g}^{-1}$ ($299.4 \text{ C} \cdot \text{g}^{-1}$) at a current density of $1 \text{ A} \cdot \text{g}^{-1}$) and excellent rate performance (75% capacitance retention at a current density of $12 \text{ A} \cdot \text{g}^{-1}$). The effect of structural regulation on the electrochemical performance of ZnMn_2O_4 nanoparticles is investigated. The purpose of this work is to propose a method to solve the problem of the low specific capacitance (specific capacity) of ZnMn_2O_4 electrode materials for supercapacitors and a new reference for designing high-performance ZnMn_2O_4 electrodes for supercapacitors.

2. Materials and Methods

In this work, all chemical reagents were purchased from Aladdin (Shanghai, China) at an analytically pure grade. The carbon cloths were purchased from Kunshan Ansu Electronic Materials (Suzhou, China). The deionized water used came from local sources. The Teflon-lined stainless-steel autoclave was purchased from Changyi Equipment (Xi'an, China). Firstly, 1 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.2975 g) and 2 mmol $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.5741 g) were dissolved into 70 mL of deionized water. Subsequently, 6 mmol urea (0.36 g) and 9 mmol NH_4F (0.3333 g) were added under continuous agitation. After 1 h, a carbon cloth ($1 \text{ cm} \times 2 \text{ cm}$) that had been heat-treated at high temperatures was soaked in the above solution. The $1 \times 1 \text{ cm}$ end of the carbon cloth was wrapped with Teflon tape to prevent the deposition of nanoparticles on the carbon cloth. Then, the carbon cloth was placed in the bottom of a 100 mL Teflon-lined stainless-steel autoclave and the above mixture was poured into the Teflon-lined stainless-steel autoclave. The Teflon-lined stainless-steel autoclave was heated in an oven under air at 120°C for 7, 9, and 12 h as hydrothermal conditions. The precipitates were collected and washed several times with ethanol and DI water. All the above precipitates were dried in an oven at 50°C overnight, and the off-white precipitates that were deposited on the carbon cloth were obtained. After calcinating in the furnace at 350°C for 3 h, the final materials were obtained, which were named ZMO-7, ZMO-9, and ZMO-12.

2.1. Material Characterization

In this work, the crystal phase of samples was analyzed by X-ray diffraction (XRD, D/max-2500 (Rigaku Corporation, Shanghai, China)). After placing the powder of the synthesized samples on the sample holder of the X-ray setup, the analysis was performed with a scan rate of 0.5° per minute in the range of $10\text{--}70^\circ$. The valence states of elements in the samples were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific, Xi'an, China). The results of XRD and XPS were used to confirm the composition of the samples. The morphology and microstructure of the samples were observed by scanning electron microscopy (SEM, JSM-7500FA (JEOL, Beijing, China)) and field emission transmission electron microscopy (FETEM, JEM-2011 (JEOL, Beijing, China)). The results of SEM and TEM were used to deduce the growth process of zinc manganate nanoparticles on the carbon cloth under different hydrothermal reaction times.

2.2. Electrochemical Measurements

The Shanghai CHI 760E Electrochemical Workstation (CH Instruments, Inc., Bee Cave, TX, USA) was used for all cyclic voltammetry (CV), galvanostatic charge–discharge (GCD), and electrochemical impedance spectroscopy (EIS) measurements. Single-electrode electrochemistry was performed on a standard three-electrode system in 2 M KOH using a Pt electrode ($1\text{ cm} \times 1\text{ cm}$) as the counter electrode and a Hg/HgO electrode as the reference electrode. ZMO-7, ZMO-9, and ZMO-12 were used directly as working electrodes. The specific capacitance (C_s) (specific capacity (C_p)) of the electrodes was calculated from the GCD test results according to the following equation:

$$C_s = \frac{I\Delta t}{m\Delta V} (C_p = \frac{I\Delta t}{m}) \quad (1)$$

where I , Δt , ΔV , and m are the discharge current, discharge time, voltage window, and mass of the active materials ZnMn_2O_4 .

The following steps were used to fabricate the AC electrode: mixtures were obtained by mixing AC, acetylene black, and poly (vinylidene fluoride) (PVDF) in a weight ratio of 7:2:1. Then, the mixtures were pressed at 10 MPa into nickel foam ($1\text{ cm} \times 1\text{ cm}$). After drying at 60°C for overnight, AC electrodes were obtained. In this work, the ASC device was assembled with ZMO-9 as a positive electrode, AC as a negative electrode, and the gel prepared by 2M KOH and polyvinyl alcohol (PVA) as the electrolyte to prevent short circuits caused by direct contact between the positive and negative materials. Electrochemical tests of the ASC device were carried out at room temperature. The optimized mass balance of the anode and cathode electrodes (m_+/m_-) was determined to be the following equation:

$$\frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+} \quad (2)$$

where m , C , and ΔV are the mass of the active material, specific capacitance, and voltage window. The energy density (E , $\text{Wh}\cdot\text{kg}^{-1}$) and the power density (P , $\text{W}\cdot\text{kg}^{-1}$) were calculated according to the following equations:

$$E = \frac{1}{2} \times \Delta V^2 \times C \quad (3)$$

$$P = \frac{E}{\Delta t} \quad (4)$$

3. Results and Discussion

The XRD technique is extensively utilized to preliminarily determine the composition of synthesized materials. In this study, XRD analysis was employed to investigate the composition of ZnMn_2O_4 deposited on carbon cloth. As shown in Figure 1a, the diffraction peaks at $2\theta = 29.4, 31.2, 36.4, 38.9, 54.3, 59.0, 60.7$, and 65.8° correspond well to the char-

acteristic diffraction pattern of ZnMn_2O_4 (JCPDS No. 24-1133). Additionally, the broad peaks at $2\theta = 25^\circ$ and 43.5° correspond to those of carbon cloth. Importantly, the absence of impurity peaks in the XRD pattern confirms the successful deposition of pure ZnMn_2O_4 following hydrothermal treatments for 7, 9, and 12 h and subsequent high-temperature sintering. XPS analysis is conducted to further confirm the composition of ZnMn_2O_4 on the carbon cloth. The total XPS peaks in Figure 1b reveal the presence of the elements C, Zn, Mn, and O. The XPS spectra of the elements provide more detailed information about their electronic states, as shown in Figure 1c,d. Specifically, Figure 1c shows the spectrum of Zn 2p, where the characteristic peaks at 1021.1 eV and 1044.2 eV correspond to Zn $2p_{3/2}$ and Zn $2p_{1/2}$, respectively. This indicates that the predominant valence state of Zn in the ZnMn_2O_4 compound was Zn^{2+} . Similarly, Figure 1d displays the fitted spectrum of Mn 2p with characteristic peaks at 641.2 eV and 653.8 eV corresponding to Mn $2p_{3/2}$ and Mn $2p_{1/2}$, respectively. These results prove that the predominant valence state of Mn in the ZnMn_2O_4 compound is Mn^{3+} . A comprehensive analysis of the XRD and XPS data leads to the conclusion that the deposition of ZnMn_2O_4 on the carbon cloth substrate was successful.

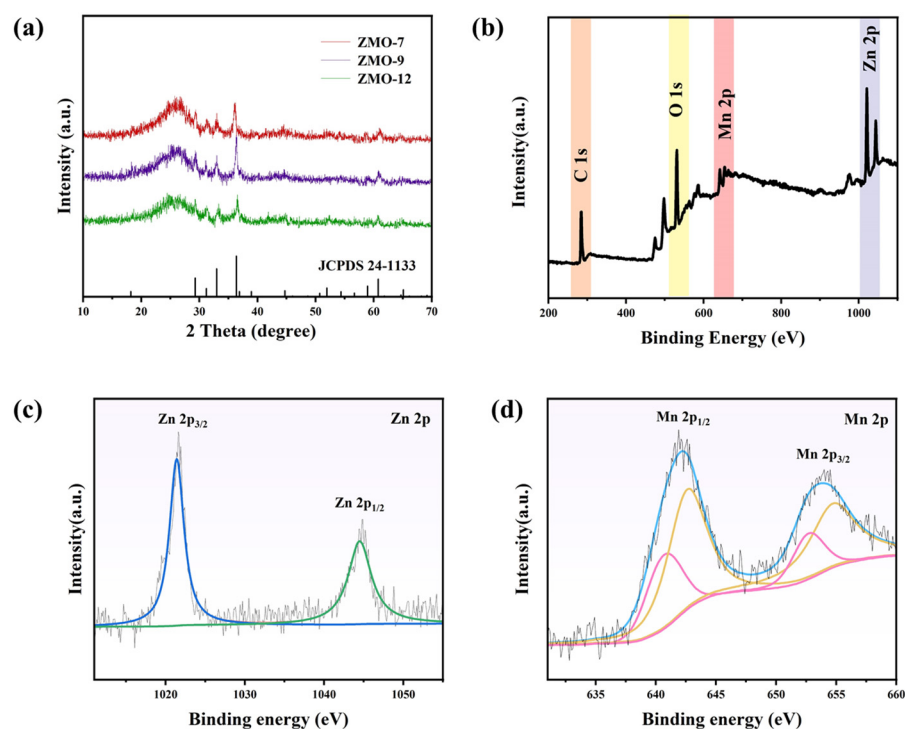


Figure 1. (a) XRD patterns of the as-prepared samples. (b) XPS full scan spectra, (c) Zn 2p, and (d) Mn 2p spectra of ZnMn_2O_4 .

SEM technology was employed to accurately determine the deposition morphology of ZnMn_2O_4 on carbon cloth and explore its deposition process. The results are presented in Figure 2. Figure 2a–c reveal that when the hydrothermal reaction time is 7 h, ZnMn_2O_4 nanoparticles are deposited on the carbon cloth in shuttle-like and spherical-like morphologies. Notably, the number of spherical-like ZnMn_2O_4 nanoparticles is larger than that of shuttle-like ZnMn_2O_4 nanoparticles, which are attached to the spherical-like nanoparticles. Figure 2d shows that shuttle-like ZnMn_2O_4 nanoparticles predominate over spherical ZnMn_2O_4 nanoparticles on the carbon cloth when the hydrothermal reaction time is 9 h. Figure 2e further reveals that the shuttle-like ZnMn_2O_4 nanoparticles possess a large pore structure in the middle, and a hollow internal structure is observable in the cross-section of the broken shuttle-like nanoparticles. When the hydrothermal reaction time is extended to 12 h, the spherical ZnMn_2O_4 nanoparticles almost disappear, and a large number of shuttle-like ZnMn_2O_4 nanoparticles are massively aggregated on the surface of the carbon

cloth. Meanwhile, it is also found that the structural integrity of the shuttle-like ZnMn_2O_4 nanoparticles is severely compromised with many broken particles intermixing with intact ones. This would be detrimental to contact with electrolyte ions for supercapacitor electrode material during electrochemical reactions. Meanwhile, severe aggregation among nanoparticles will lead to an inferior binding force between the nanoparticles and carbon cloth. Therefore, the nanoparticles easily detach from the carbon cloth during the electrochemical cycle, leading to unsatisfactory cycle stability. The results of SEM image analysis show that spherical ZnMn_2O_4 nanoparticles may gradually convert into shuttle-like ZnMn_2O_4 nanoparticles as the hydrothermal reaction time extends. More studies have focused on the preparation of TMO nanoparticles, ignoring the aggregation phenomenon caused by the uneven distribution of nanoparticles, which reduces the electrochemical performance of the electrode materials. For example, Zuo et al. prepared ZnMn_2O_4 hollow microspheres that exhibit the specific capacitance of $442.91 \text{ F}\cdot\text{g}^{-1}$ at a current density of $1 \text{ A}\cdot\text{g}^{-1}$ [20]. It can be seen from the SEM images in this study that the aggregation among the microspheres was one of the main reasons for the unsatisfactory specific capacitance. From the SEM image analysis in our work, it can be seen that the deposition of ZnMn_2O_4 nanoparticles on carbon cloth can effectually achieve a uniform distribution by controlling the hydrothermal reaction time, which was different from the direct hydrothermal preparation of ZnMn_2O_4 . This characteristic facilitates an increase in the contact area between the electrolyte and the active material during the electrochemical reaction and improves the specific capacitance of the electrode material.

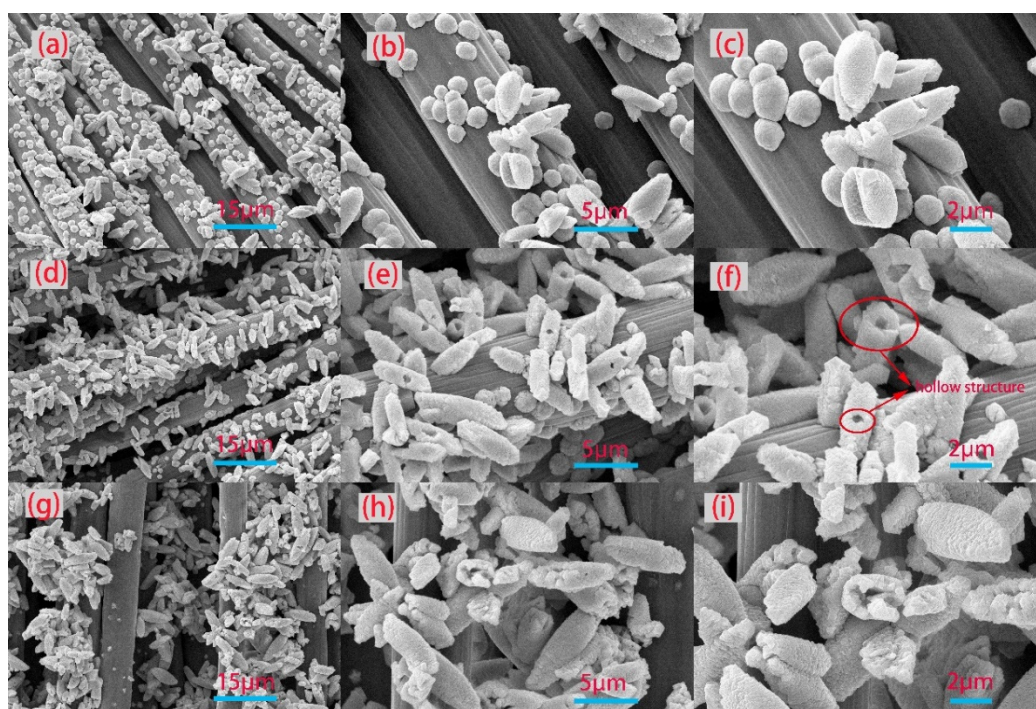


Figure 2. SEM images of ZnMn_2O_4 with different hydrothermal reaction times: hydrothermal reaction times of 7 h (a–c), 9 h (d–f), and 12 h (g–i).

To further investigate the impact of the hydrothermal reaction time on the morphology of ZnMn_2O_4 nanoparticles deposited on the carbon cloth, TEM technology was utilized, and the results are shown in Figure 3. The lattice images from Figure 3i–l indicate the successful synthesis of ZnMn_2O_4 nanoparticles after hydrothermal reactions of 7, 9, and 12 h followed by high-temperature calcination, corroborating the XRD and XPS results. Figure 3a,b display the morphological features of the ZMO-7 nanoparticles, revealing the ZMO-7 nanoparticles' own spherical-like and shuttle-like morphologies. Further magnification (Figure 3e,f) shows that the edges of the ZMO-7 nanoparticles have thin nanosheet

structures, suggesting that spherical and shuttle-like ZMO-7 nanoparticles may be assembled from nanosheets. Also combining Figure 3b, a small exclusion-like indentation in the middle of the shuttle-like ZMO-7 nanoparticles can be seen. After 9 h of hydrothermal reaction and high-temperature calcination, Figure 3c,g reveal that the indentation in the shuttle-like ZMO-9 nanoparticles enlarged. The combination of Figure 3d,h shows that after 12 h of hydrothermal reaction and high-temperature sintering, the indentation size in the middle of the shuttle-like ZMO-12 nanoparticles further increased compared with that of the ZMO-9 nanoparticles, revealing a visible hollow structure. Based on the SEM and TEM analyses, it is hypothesized that the shuttle-like ZMO-12 nanoparticles deteriorated in structural stability because of the large size of the openings and depressions in the middle. Therefore, we can infer that ZMO-12 nanoparticles are prone to structural collapse after a long hydrothermal process with high-temperature sintering.

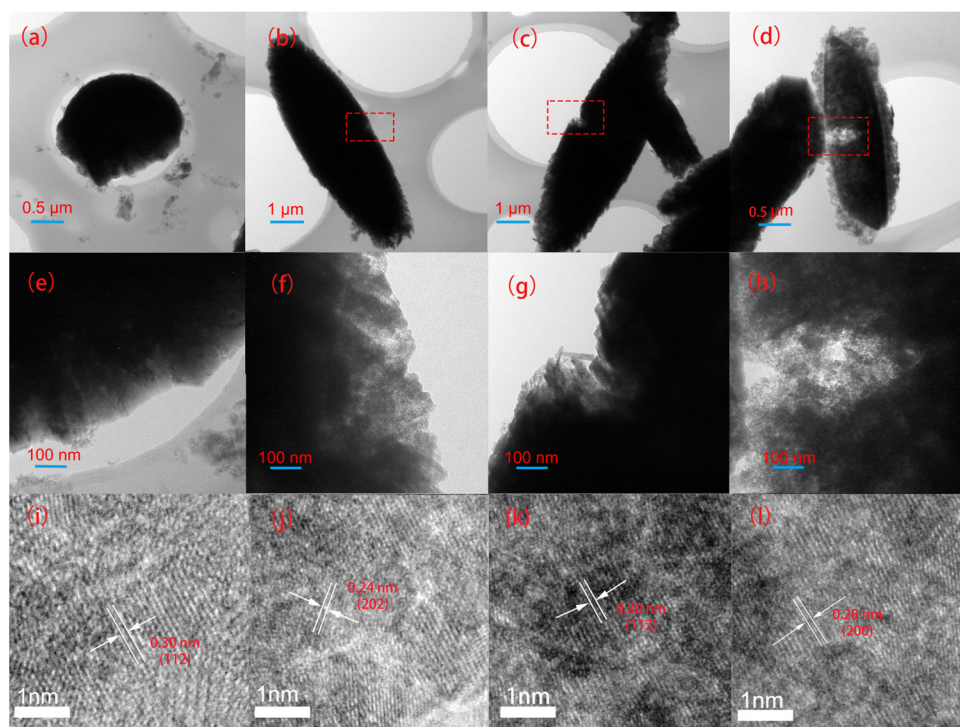


Figure 3. TEM images of ZnMn_2O_4 with different hydrothermal reaction times: hydrothermal reaction time of 7 h (a,b,e,f,i,j), 9 h (c,g,k), and 12 h (d,h,l).

The deposition process of ZnMn_2O_4 on carbon cloth can be deduced by integrating the SEM and TEM results. Zn^{2+} and Mn^{2+} combine with CO_3^{2-} produced by urea under high-temperature and precursor nanoparticles assemble during the 7 h hydrothermal process to potentially form nanosheet-like metal hydroxides, as shown in Figure 4. These gradually assemble into spherical ZMO-7 nanoparticles on the carbon cloth because of thermodynamic stability principles [21,22]. As the reaction continues, the nanosheets are further assembled and grown on the spherical-like ZMO-7 nanoparticles to form shuttle-like ZMO-7 nanoparticles with spherical-like ZMO-7 nanoparticles acting as substrate. The limited hydrothermal reaction time results in more spherical-like ZMO-7 nanoparticles than shuttle-like ZMO-7 nanoparticles. After extending the hydrothermal reaction time to 9 h, the spherical ZMO-9 nanoparticles on the carbon cloth are reduced to more shuttle-like ZMO-9 nanoparticles, which indicates that more nanosheets are assembled and grown into shuttle-like ZMO-9 nanoparticles. When the reaction time is extended to 12 h, shuttle-like ZMO-12 nanoparticles are predominantly deposited on the carbon cloth and show significant aggregation. A prolonged hydrothermal time can influence the structural stability of the nanoparticles, leading to more damaged structures in ZMO-12 nanoparticles.

During high-temperature calcination, the Kirkendall effect primarily accounts for the hollow structure in all shuttle-like nanoparticles [23]. The different diffusion rates of Zn^{2+} and Mn^{2+} during oxidation create surface roughness on ZnMn_2O_4 nanoparticles. The deposition of ZMO-9 nanoparticles on the carbon cloth is more uniform, and the structures are complete. The uniform distribution and structural integrity of the nanoparticles on the carbon cloth are related to the control of the hydrothermal reaction time. Consequently, ZMO-9 nanoparticles may exhibit the best electrochemical performance as an electrode material for supercapacitors compared with ZMO-7 and ZMO-12 nanoparticles.

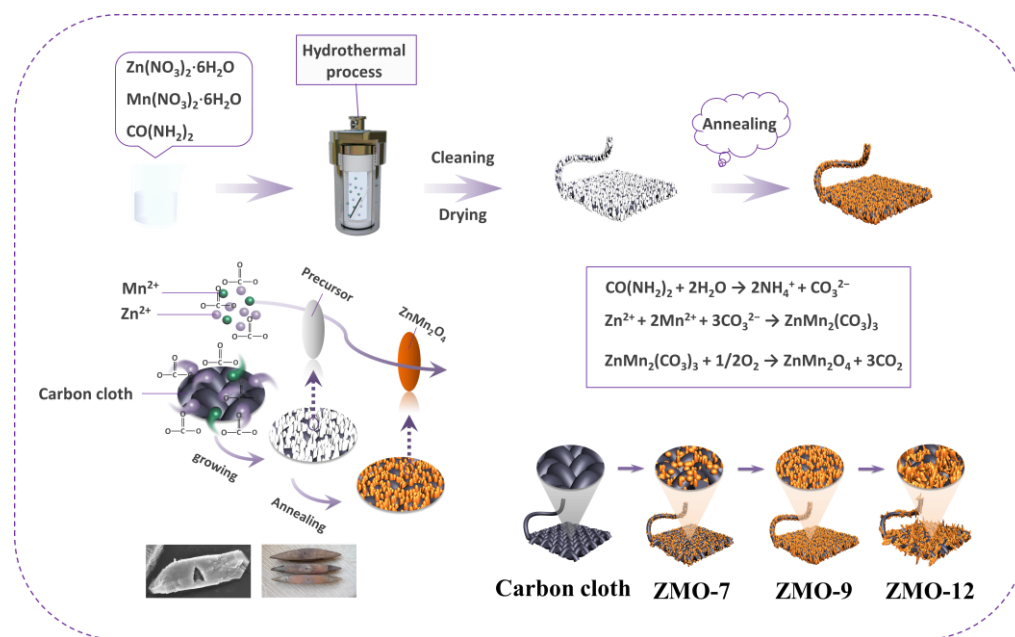
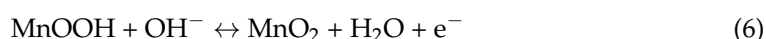


Figure 4. Schematic illustration of the fabrication process of ZnMn_2O_4 @carbon cloth.

The morphology and structure of electrode materials are some of the key factors that determine the electrochemical performance of supercapacitors. This is because, in the electrochemical reaction of supercapacitors, the energy storage process of the electrode material is related to the reactivity and ion and electron transport rates [24]. The morphology and structure of the electrode material can be designed to increase the contact area between the electrode material and the electrolyte so that the specific capacitance (specific capacity) of the electrode material can be increased [25]. In this work, the deposition morphology of ZnMn_2O_4 nanoparticles on carbon cloth under different hydrothermal reaction times was studied first. From the combination analysis of SEM and TEM images, it can be seen that ZMO-7 nanoparticles are evenly distributed on the carbon cloth and have low aggregation, which provides a shortcut for their contact with electrolytes during electrochemical reactions. However, most of the deposition morphology of the ZMO-7 nanoparticles on the carbon cloth is spherical-like nanoparticles and the internal structure is solid, which hinders the diffusion of electrolytes in the active material during the electrochemical reaction. When the ZMO-9 nanoparticles are deposited on the carbon cloth with uniform distribution, its microstructures present a hollow structure with openings, which greatly improves the diffusion rate of the electrolyte inside the electrode material during the electrochemical reaction and expands the contact area between the electrolyte and the active material, improving the specific capacitance of electrode materials. Although ZMO-12 nanoparticles also have a hollow structure, the combination of SEM and TEM image analysis results shows that a large number of ZMO-12 nanoparticles accumulate, and even the nanoparticles produce different degrees of damage, which greatly reduces the chances of full contact between the electrolyte and the active substance during the electrochemical reaction. At the same time, a large amount of aggregation will also make

the binding force of the ZMO-12 nanoparticles and carbon cloth worse, so that ZMO-12 nanoparticles are more likely to fall off the carbon cloth compared with ZMO-7 and ZMO-9 in the case of electrochemical cyclic charging and discharging for long time, resulting in the deterioration of cycle performance.

To validate the aforementioned hypothesis, three-electrode tests are employed using the prepared ZMO-7, ZMO-9, and ZMO-12 as binder-free electrode materials, as shown in Figure 5. Firstly, the CV curves of carbon cloth, ZMO-7, ZMO-9, and ZMO-12 electrodes are presented in Figure 5a at a scan rate of $5 \text{ mV} \cdot \text{s}^{-1}$. It is evident from Figure 5a that the curve area of the ZMO-9 electrode is larger than those of the carbon cloth and the ZMO-7 and ZMO-12 electrodes, indicating that the ZMO-9 electrode possesses the best specific capacitance. The area of the CV curve is related to the electrochemical surface area of the electrode material. Therefore, the larger contact area between the electrolyte and electrode material represents the more active sites that undergo redox reactions during the electrochemical reaction, resulting in a greater amount of charge generated, showing a larger area of the CV curve [26–28]. Combined with the results of the ZMO-9 and ZMO-12 electrode morphology analysis, it can be observed that although both ZMO-9 and ZMO-12 have shuttle-like structures, the distribution of ZMO-9 nanoparticles on the carbon cloth is more uniform, which will be favorable to the contact between the electrolyte and ZMO-9 nanoparticles during the electrochemical reaction and fully activate the active site of the active material. However, ZMO-12 nanoparticles produce a serious accumulation phenomenon on the carbon cloth, which prevents full contact between the electrolyte and the active material during the electrochemical reaction, so more active sites are covered. Therefore, it can be observed that the ZMO-9 electrode has a larger CV curve area than the ZMO-12 electrode in the CV test. Figure 5b shows CV curves at various scan rates for the ZMO-9 electrode to evaluate its electrochemical properties. We can observe that as the scan rate increases, the peak current also increases. This might be explained by the fact that a higher current rate lowers the resistance by lowering the diffusion layer. In addition, the redox peaks gradually shift with increasing scan rates, primarily because of increased diffusion resistance and polarization phenomena [29–31]. At a scan rate of $5 \text{ mV} \cdot \text{s}^{-1}$, the peak at 0.35 V represents the oxidation process of the electrode material, while the peak at 0.44 V indicates the reduction reaction process of the electrode material. The detailed electrochemical reaction processes are as follows [32]:



It can be supposed from the electrochemical reaction processes that the contact area between the electrode material and OH^- in the electrolyte and the electron transport rate plays a crucial role in the specific capacitance of the electrode materials [33]. Therefore, the shuttle-like ZMO-9 nanoparticles with a uniform distribution and stable structure on the carbon cloth can provide a larger contact area with electrolyte ions and improve the electron transport rates [34]. Therefore, the ZMO-9 electrode is hypothesized to have the best specific capacitance. To further verify the above inference, the discharge curves of ZMO-7, ZMO-9, and ZMO-12 electrodes at a current density of $1 \text{ A} \cdot \text{g}^{-1}$ are shown in Figure 5c. In Figure 5c, it can be observed that the discharge curves of the ZMO-7, ZMO-9, and ZMO-12 electrodes at a current density of $1 \text{ A} \cdot \text{g}^{-1}$ show a significant deviation from a straight and flat line, and the galvanostatic discharge curves appear as a distinct plateau region. It can be seen through the combination of this phenomenon and the CV curve analysis that capacitance mainly comes from faradaic redox reactions with battery-like behavior. The specific capacitance (specific capacity) of the ZMO-7, ZMO-9, and ZMO-12 electrodes at a current density of $1 \text{ A} \cdot \text{g}^{-1}$ is calculated as 246, 499, and $100 \text{ F} \cdot \text{g}^{-1}$ (147.6 , 299.4 , and $60 \text{ C} \cdot \text{g}^{-1}$), respectively. Distinctly, the ZMO-9 electrode has optimal specific capacitance (specific capacity), aligning with the CV curves and SEM and TEM analysis

results. The results compared with other studies are shown in Table 1. It can be seen that the ZMO-9 electrode has excellent specific capacitance (specific capacity).

Table 1. Comparison of the specific capacitance (specific capacity) of different supercapacitor electrodes.

Electrode	Specific Capacitance	Scan Rate/Current Density	Reference
ZnMn ₂ O ₄ /MWCNT	103 F·g ^{−1}	1 mV·s ^{−1}	[35]
birnessite-type MnO ₂	252.2 F·g ^{−1}	0.5 A·g ^{−1}	[36]
ZnMn ₂ O ₄ /Mn ₂ O ₃	380 F/g	0.5 A·g ^{−1}	[37]
MnFe ₂ O ₄	227 F·g ^{−1}	2 A·g ^{−1}	[38]
Fe ₂ O ₃ @MnO ₂	449 F·g ^{−1}	1 A·g ^{−1}	[39]
ZnCo ₂ O ₄ -rGO	359 F·g ^{−1}	0.5 A·g ^{−1}	[40]
ZMO-9	499 F·g ^{−1}	1 A·g ^{−1}	This work

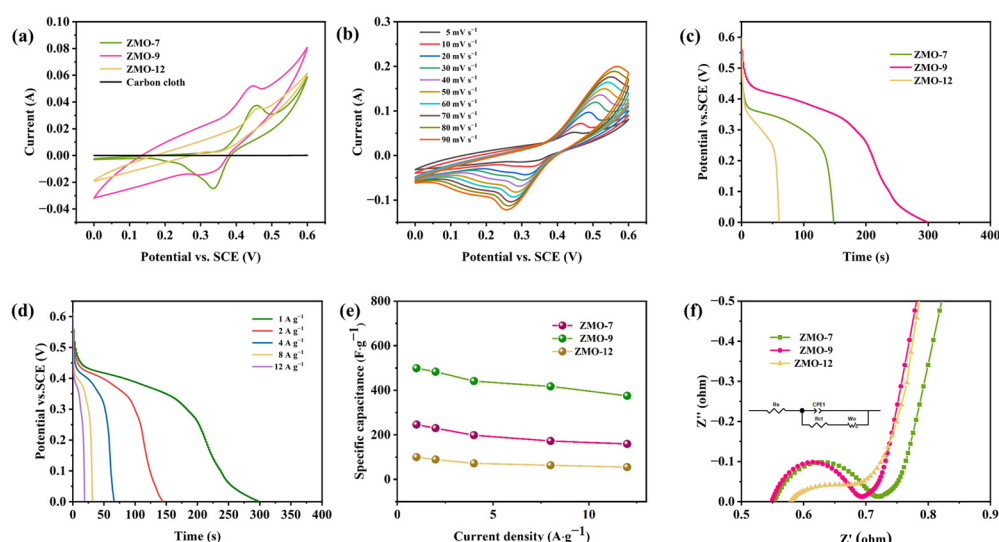


Figure 5. (a) CV curves at the scan rate of 5 mV·s^{−1}. (b) CV curves of the ZMO-9 electrode at a scan rate of 5 mV·s^{−1} to 90 mV·s^{−1}. (c) GCD curves at a current density of 1 A·g^{−1}. (d) GCD curves at different current densities of the ZMO-9 electrode. (e) Comparison of the specific capacitance change. (f) The fitting EIS curves of the ZMO-7, ZMO-9 and ZMO-12 electrodes.

The discharge curves of the ZMO-9 electrode at different current densities are shown in Figure 5d, and the distinct voltage platforms confirm the pseudocapacitive behavior of the ZMO-9 electrode [41]. The shortening of the discharge time with increasing current density is due to the lack of time for electrolyte ions to adsorb onto the surface of the electrode material as a result of dynamic confinement at high current densities, leading to a gradual weakening of the voltage plateau and a tendency for the curve to become triangular [42,43]. The specific capacitance (specific capacity) of the ZMO-9 electrode at different current densities can be calculated, and the results are exhibited in Figure 5e. When the current density increases from 1 A·g^{−1} to 12 A·g^{−1}, the specific capacitance (specific capacity) of the ZMO-7, ZMO-9, and ZMO-12 electrodes decreases to varying extents because of charge transfer difficulties and insufficient contact with electrolyte ions at high current densities [44]. When the current density is increased from 1 A·g^{−1} to 12 A·g^{−1}, the specific capacitance (specific capacity) of the ZMO-7, ZMO-9, and ZMO-12 electrodes remained at 65%, 75%, and 55%, respectively, indicating that the ZMO-9 electrode had the best rate performance. To further explore the electrochemical performance of electrode materials in this work, EIS tests were used to obtain the resistance information of the electrode materials. The fitting EIS curves based on the ZMO-7, ZMO-9, and ZMO-12 electrodes are shown in Figure 5f. The semicircle of the curve represents charge transfer resistance (R_{ct}) and the

X-intercept represents the equivalent series resistance (R_s). The fitting results of R_s for the ZMO-7, ZMO-9, and ZMO-12 electrodes are 0.57, 0.56, and 0.59, respectively. In addition, the fitting results of R_{ct} for the ZMO-7, ZMO-9, and ZMO-12 electrodes are 0.14, 0.12, and 0.20, respectively. Without the involvement of a binder, the resistance of the overall electrode material is reduced, which is more conducive to the transfer of electrons and charge. The main reason for the significantly higher R_{ct} of the ZMO-12 electrode than that of the ZMO-7 and ZMO-9 electrodes is due to the accumulation of ZMO-12 nanoparticles resulting in impeded diffusion of the electrolyte in the ZMO-12 electrodes, which leads to the difficulty of charge transfer.

To further confirm the charge storage mechanism, quantitative analyses were employed based on the CV curve at a scan rate of 5, 10, 20, 40, and 60 $\text{mV}\cdot\text{s}^{-1}$ to study the kinetical features of the ZMO-9 electrode. The power law was used to estimate the charge storage process of the ZMO-9 electrode according to Equations (7) and (8) as follows [45]:

$$i = av^b \quad (7)$$

$$\log i = b \log v + \log a \quad (8)$$

where i and v are the redox peak current and corresponding scan rate, respectively. In Figure 6a, the value of $\log a$ can be confirmed from the horizontal intercept, and the value of b can be calculated from the slope of the fitting straight line. It is worth noting that if the value of b is 0.5, then the electrochemical kinetics reaction of the electrode is a diffusion-controlled process. If the value of b is 1, it indicates a surface faraday redox reaction. A value of b between 0.5 and 1 is related to the diffusion and surface control process of an electrode [46]. Therefore, the b values of the ZMO-9 electrode are calculated to be 0.55 and 0.83, respectively. The results indicate that the dominant charge storage mechanism of the ZMO-9 electrode is a mixed surface faradaic redox reaction mechanism with the battery mechanism. Hence, the CV and GCD curves of the ZMO-9 electrode show remarkable characteristics of battery-like materials. In addition, the capacitive contribution and the diffusion contribution can be determined quantitatively by calculating their respective proportions as follows:

$$i(V) = k_1v + k_2v^{1/2} \quad (9)$$

$$i(V)/v^{1/2} = k_1v^{1/2} + k_2 \quad (10)$$

where i , k_1v , and $k_2v^{1/2}$ represent the current at fixed voltage, capacitive-controlled processes, and diffusion-controlled processes, respectively. Based on Equations (9) and (10), k_1 and k_2 can be obtained by the slope and the y -axis intercept of a straight line at each given voltage. Several specific voltages (V , mV) and k_1v (i , mA) are connected through smooth curves for nonlinear fitting, and then the area of the fitted closed curve is integrated to obtain the area of the CV curve under a specific scanning rate. The value can be obtained by dividing the area of the fitted curve by the area of the CV curve, which is the capacitive contribution rate at a specific scanning rate. As shown in Figure 6b, the capacitive contribution at 10 $\text{mV}\cdot\text{s}^{-1}$ was calculated to be 70%. With the scanning speed increasing from 5 $\text{mV}\cdot\text{s}^{-1}$ to 60 $\text{mV}\cdot\text{s}^{-1}$, the capacitive contribution of the ZMO-9 electrode is calculated to be 61% and 83%, as shown in Figure 6c. The results show that the diffusion process is limited, especially at high scan rates, suggesting that the capacitive process is an important component of charge storage; thus, the ZMO-9 electrode has good cycling stability. Long-cycle testing at a current density of 1 $\text{A}\cdot\text{g}^{-1}$ over 6000 cycles shows that the ZMO-7, ZMO-9, and ZMO-12 electrodes retain 70%, 90%, and 50% of their initial specific capacitances (specific capacity), respectively. In this work, ZnMn_2O_4 nanoparticles are deposited directly on carbon cloth, although a uniform distribution of nanoparticles is achieved to prevent the problem of specific capacitance (specific capacity) reduction caused by aggregation. However, the ZMO-7, ZMO-9, and ZMO-12 electrodes prepared with different hydrothermal reaction times still showed different degrees of specific capacitance (specific capacity) attenuation during the long-cycle reaction process. The main reason for

the worst cycle stability of the ZMO-12 electrode is that the active materials are more likely to fall off during the long-cycle charging and discharging process because of the accumulation of a large number of nanoparticles. Based on previous analyses [47–49], the reasons for the attenuation of the specific capacitance (specific capacity) of electrode materials during the long cycle may be summarized as the following two points: (1) ZnMn_2O_4 nanoparticles are deposited directly on the carbon cloth, and the inferior interaction force between the ZnMn_2O_4 nanoparticles and the carbon cloth causes the ZnMn_2O_4 nanoparticles to fall off easily during the long cycle, resulting in the decline of cycle stability. (2) ZnMn_2O_4 nanoparticles, as active materials, undergo repeated redox reactions in the process of long-term cyclic charge–discharge reactions, which causes different degrees of dissolution and structural collapse of the active materials, thus reducing the active materials involved in the electrochemical reaction and hindering the full contact between the electrolyte and the active materials. In this work, we adjusted the hydrothermal reaction time from the perspective of material structure design and distribution and combined it with the results of the cycle stability test, which summarized that a suitable hydrothermal reaction time can construct uniformly distributed ZMO-9 electrode materials with favorable cycle stability on carbon cloth. However, to improve the cycle stability of ZMO-9 electrode materials based on the combination of the above analysis of specific capacitance attenuation during the long cycle of the electrode material, future work will focus on the following two points that are expected to improve the cycle stability of the ZMO-9 electrode: (1) By modifying the carbon cloth, such as introducing active groups on the surface of the carbon cloth and etching the carbon cloth to increase its surface roughness, the binding force between ZMO-9 nanoparticles and the carbon cloth can be strengthened, improving the cyclic stability of the electrode material. (2) Surface modification of ZMO-9 nanoparticles can be carried out to limit the structural collapse and dissolution caused by volume expansion and contraction of ZMO-9 during cycle charging and discharge.

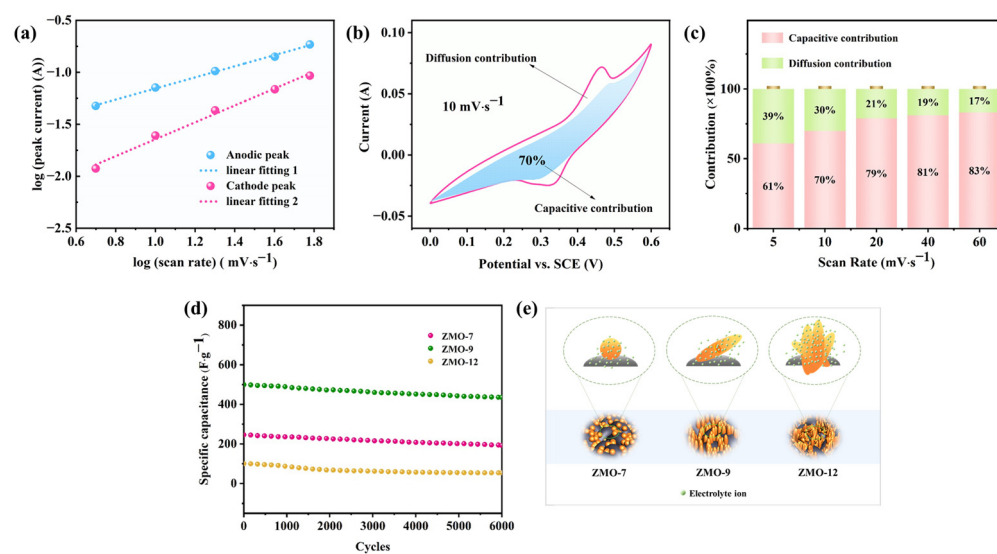


Figure 6. (a) Determination of the b-value from the anodic and cathodic peak currents using the power law. (b) Capacitance contribution at $10 \text{ mV}\cdot\text{s}^{-1}$. (c) The capacitance contribution ratio at different scan rates. (d) Long-cycle performance of the ZMO-7, ZMO-9, and ZMO-12 electrodes at $1 \text{ A}\cdot\text{g}^{-1}$. (e) Diagram of contact between the electrolytes and electrode materials.

Combining the above electrochemical test and analysis results and Figure 6e, we summarize the influence of the deposition distribution and morphologies of ZnMn_2O_4 nanoparticles on the carbon cloth on the electrochemical performance as follows: In this work, we achieved the deposition of ZnMn_2O_4 nanoparticles on the carbon cloth by controlling the hydrothermal reaction time. The deposition distribution and morphologies of the ZnMn_2O_4 nanoparticles on the carbon cloth are different because of the difference in

the hydrothermal time. Electrode materials are one of the key factors that determine the electrochemical performance of supercapacitors, and different compositions and morphologies have different effects on the charge storage of electrode materials in the electrochemical reaction processes and the contact between electrolyte and active material, thus affecting the specific capacitance (specific capacity) of electrode materials. The results of SEM and TEM image analyses and the electrochemical performance test show that ZMO-9 electrodes have more uniform nanoparticle distribution and the best electrochemical performance. As shown in Figure 6e, when the ZnMn_2O_4 nanoparticles with different distribution and morphologies, prepared according to different hydrothermal reaction times, were in contact with electrolyte ions, ZMO-7 nanoparticles with spherical-like structure and shuttle-like ZMO-9 nanoparticles can make full contact with electrolyte ions, and the active sites are fully utilized. However, the accumulation of ZMO-12 nanoparticles with shuttle-like structure makes it difficult for electrolyte ions to achieve full contact with the ZMO-12 nanoparticles, resulting in a lot of “dead volume” at the active sites of the ZMO-12 electrode, so the ZMO-12 electrode shows the lowest specific capacitance (specific capacity) compared with the ZMO-7 and ZMO-9 electrodes. The main reason that the specific capacitance (specific capacity) of the ZMO-7 electrode is lower than that of the ZMO-9 electrode is that ZMO-9 nanoparticles have an open hollow structure, which makes the contact area between electrolyte ions and the active material larger than that of solid ZMO-7 nanoparticles. Secondly, because of the limitation of the hydrothermal reaction time, a lower amount of ZMO-7 nanoparticles as active materials are deposited on the carbon cloth, so the reduction in active sites in the process of electrochemical reaction also leads to the inferior specific capacity. At the same time, compared with ZMO-7 and ZMO-12 nanoparticles, the open hollow shuttle-like structure of ZMO-9 nanoparticles also provides a convenient contact interface for the contact between electrolyte ions and active materials under high current density, thus improving the rate performance of electrode materials. In addition, the difference in deposition distribution of nanoparticles on carbon cloths caused by different hydrothermal reaction times also affects the cyclic stability of electrode materials. Therefore, the ZMO-12 electrode with severe nanoparticle aggregation has the worst cycle stability because of the weak binding force between the nanoparticle and the carbon cloth.

To further evaluate the practical utility of the ZMO-9 electrode, this work engineered a ZMO-9//AC ASC device. Figure 7a shows the CV curves of the ZMO-9//AC device with scan rates ranging from 10 to 100 $\text{mV}\cdot\text{s}^{-1}$. The CV curves show prominent redox peaks, as shown in Figure 7a, which are a distinctive feature of the synergistic combination of electric double-layer capacitive electrodes and Faradaic redox electrodes. As the CV scan rate increases, the oxidation peak shifts to the right. But the overall shape of the CV curves remains relatively stable, indicating that the system maintains its stability even at higher scan rates. Figure 7b presents the GCD curves obtained at various current densities ranging from 1 to 10 $\text{A}\cdot\text{g}^{-1}$. Based on the GCD curves, we analyzed the capacitance and charge–discharge characteristics of the device, enabling the calculation of the ASC device’s specific capacitance. Figure 6c illustrates the specific capacitance at various current densities. The device achieves a specific capacitance of $131.2 \text{ F}\cdot\text{g}^{-1}$ at a current density of $1 \text{ A}\cdot\text{g}^{-1}$, which decreases to $91.9 \text{ F}\cdot\text{g}^{-1}$ at a current density of $10 \text{ A}\cdot\text{g}^{-1}$, retaining 70% of its specific capacitance. The stability of the ZMO-9//AC device was tested, and the results are exhibited in Figure 7e. As shown in Figure 6e, cycling stability tests conducted at a current density of $5 \text{ A}\cdot\text{g}^{-1}$ indicate that the ZMO-9//AC device retains 60% of its initial specific capacitance after 5000 cycles, portending the stability and potential for long-time application of the ZMO-9//AC device in energy storage technologies. In Figure 7f, the energy and power densities of the ZMO-9//AC device are calculated to be 46.6, 44.2, 42.3, 40.6, 39.1, and 32.7 $\text{Wh}\cdot\text{kg}^{-1}$, corresponding to power densities of 800.1, 1600.6, 2400.5, 3201.4, 4000, and 8002.2 $\text{W}\cdot\text{kg}^{-1}$, respectively. The results are superior to other supercapacitor devices shown in Figure 7f. All the results demonstrate that the shuttle-like ZMO-9 nanoparticles that were deposited on the carbon cloth and prepared by adjusting the hydrothermal reaction time and calcination at a high temperature have excellent specific

capacitance and rate performance when used as electrode materials for supercapacitors. This was mainly due to the control of the deposition process of ZnMn_2O_4 nanoparticles on the carbon cloth to control the morphology of the ZnMn_2O_4 nanoparticles.

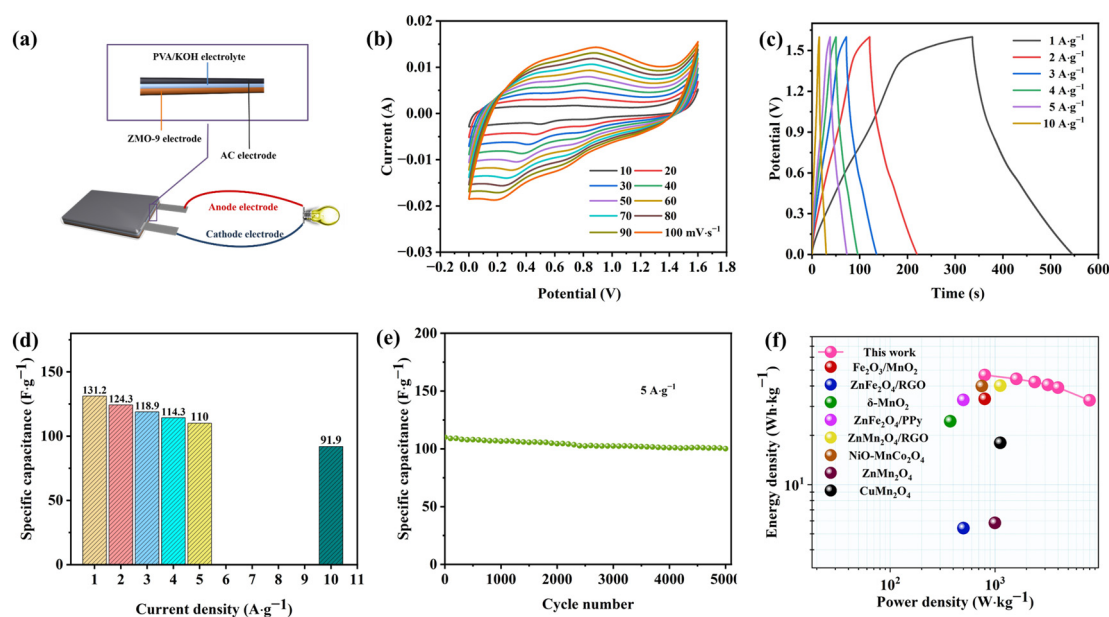


Figure 7. (a) A schematic diagram of the ZMO-9//AC device. (b) CV curves of the ZMO-9//AC device with scan rates ranging from 10 to 100 $\text{mV}\cdot\text{s}^{-1}$. (c) GCD curves at various current densities. (d) The specific capacitance at various current densities. (e) The cycling stability of the ZMO-9//AC device. (f) The energy and power densities of the ZMO-9//AC device and other devices [39,50–56].

4. Conclusions

After the hydrothermal reaction and high-temperature calcination process, ZnMn_2O_4 nanoparticles were deposited on carbon cloth in this work. The hydrothermal reaction time is the key factor affecting the deposition morphologies and distribution of ZnMn_2O_4 nanoparticles on the carbon cloth. SEM and TEM test results show that ZMO-9 has the best hollow shuttle structure and is uniformly distributed on the carbon cloth. These unique morphologies allow ZnMn_2O_4 nanoparticles to contact the electrolyte fully during the electrochemical reaction and can effectively inhibit volume expansion during charge and discharge. Therefore, the electrochemical test results of the ZMO-9 electrode show that it has high specific capacitance (specific capacity), excellent rate performance, and a long cycle life. The results show that the combination of ZnMn_2O_4 nanoparticles and the carbon cloth can improve the conductivity of the electrode materials. Controlling the morphologies and distribution of ZnMn_2O_4 nanoparticles by controlling the hydrothermal reaction time can effectively improve the electrochemical performance of ZnMn_2O_4 -based electrode materials. This work optimized the electrochemical performances of the ZnMn_2O_4 electrode materials by adjusting the structure of the ZnMn_2O_4 nanoparticles, thus providing a reference for the application of ZnMn_2O_4 in the field of supercapacitors.

Author Contributions: Conceptualization, C.L. and X.F.; methodology, X.F. and J.Z.; software, H.Y. (Huan Yu) and H.Y. (Huabing Yang); validation, C.L. and H.Y. (Huabing Yang); formal analysis, G.Z. and K.C.; investigation, K.C. and X.W.; resources, G.Z. and X.W.; data curation, H.Y. (Huan Yu) and D.Z.; writing—original draft preparation, X.F. and J.Z.; writing—review and editing, X.F.; visualization, H.Y. (Huan Yu) and H.L.; supervision, H.L. and D.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the engineering basic research project of the Qilu University of Technology (Shandong Academy of Sciences) (Grant No. 2023PX069); the Shandong Province Key Research and Development Plan (Grant Nos. 2021CXGC010303 and 2023CXGC010309); the

Talent research project of Qilu University of Technology (Shandong Academy of Sciences), project number 2023RCKY005 and 2023RCKY018; the major innovation project for integrating the science, education, and industry of the Qilu University of Technology (Shandong Academy of Sciences) (Grant Nos. 2022JBZ01-07 and 2023JBZ01); and Several Policies on Promoting Collaborative Innovation and Industrialization of Achievements in Universities and Research Institutes (Grant No. 2021GXRC126).

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Conflicts of Interest: The authors declare no conflicts of interest.

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