Rational Design for Mn_3O_4 @carbon Foam Nanocomposite with 0D@3D Structure for Boosting Electrochemical Performance

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Abstract

A rational strategy was developed to prepare a nanocomposite with 0D/3D architecture. The composite containing Mn_3O_4 nanoparticles (0D) and carbon foam (3D) could be applied as an electrode material for supercapacitor by taking advantage of high conductivity of carbon foam (CF) and high pseudocapacitance of Mn_3O_4 nanoparticles. CF was prepared by a carbonization method using melamine foam, and then Mn_3O_4 nanoparticles were combined with carbon foam by a one-step hydrothermal method to prepare $\text{Mn}_3\text{O}_4@\text{CF}$ nanocomposite. The 0D@3D hierarchical structure of $\text{Mn}_3\text{O}_4@\text{CF}$ nanocomposite using CF as a 3D growing skeleton prevents agglomeration and increases reactive sites of Mn_3O_4 nanoparticles. In addition, CF as a conductive skeleton shortens the charge transfer path. The synergistic effect between CF and Mn_3O_4 improves the electrochemical performance of CF. Three $\text{Mn}_3\text{O}_4@\text{CF}$ composites were prepared by adjusting the mass of the reactants in the processes of hydrothermal reaction. The Mn_3O_4 nanoparticles are uniformly grown on the CF surface with a diameter of 18 nm. $\text{Mn}_3\text{O}_4@\text{CF}$ -2 composite has a specific capacitance of 212.8 F/g at a current density of 1 A/g, which is much higher than that of pristine CF (79.1 F/g) and Mn_3O_4 (112.7 F/g). The cyclic stability of $\text{Mn}_3\text{O}_4@\text{CF}$ -2 is retained as 86.1% of initial capacitance after 2000 cycles at the current density of 1 A/g. It proves the feasibility of the as-mentioned strategy and broadens the application of carbon foam in supercapacitor.

1. Introduction

In recent years, the energy crisis has attracted more and more attention. The sustainable development of new energy vehicles and mobile electronic devices requires energy storage devices to put forward higher requirements in miniaturization and energy density and power density improvement. Supercapacitors, which can far exceed ordinary capacitors and electrochemical cells in energy density and power density respectively, have become a hot spot in energy storage field. Meanwhile, supercapacitors have the advantages of fast charging and discharging speed, long cycle life, low pollution and high safety [1–5]. The specific capacitance and conductivity properties of electrode materials play an important role in the electrochemical performance of supercapacitors. Among many electrode materials, carbon foam (CF) with three-dimensional skeleton [7–16] has an interconnected electronic channel, which greatly improves the electrochemical performance of the electrode compared with that of one-dimensional and two-dimensional carbon materials.

As an electrode material, CF has been widely studied. Zhang et al. [6] prepared N-doped 3D porous CF at different temperatures by a one-step carbonization method using melamine foam (MF) as raw material. By controlling the temperature, it is found that the resistance of CF in the 2 M KOH electrolyte is very low, and the resistance decreases when the carbonation temperature increases. The specific capacitance can still maintain 96% of the maximum specific capacitance after 5000 cycles. The symmetrical supercapacitor assembled with CF as electrode material can have the highest energy density of 9.34 Wh/kg at the power density of 6.9 kW/kg. Xiao et al. [9] carbonized the commercial MF to prepare a self-

supporting N-doped carbon foam (NCF) with lightweight, interconnected 3D network and rich nitrogen content. On the benefit of its excellent structural flexibility and high porosity, NCF can withstand up to 80% of the compression strain without significantly reducing its volume after 100 cycles. When exposed to the current density of 1 mA/cm² and the electrolyte of 5 M LiCl, the NCF electrode material shows the area capacitance of 332 mF/cm² and the mass ratio capacitance of 52 F/g. All-solid symmetric supercapacitor devices with NCF electrode can resist 60% strain without significant electrochemical performance change. Although MF carbonization can obtain CF with excellent mechanical properties and very low resistance, the further application of CF is greatly limited because CF still has a low specific capacitance. In order to overcome this limitation, two main strategies are as follows: one is to design the material structure and prepare the hierarchical composite as nano-material@micron-material. Cheng et al.^[10] combined 2D carbon nanosheets with CF by dipping and annealing at high temperature. The performance of supercapacitors based on this composite was significantly improved, and the specific capacitance at the current density of 1 A/g and 10 A/g was as high as 364 F/g and 321.86 F/g, respectively. Another is to obtain additional pseudo-capacitance by means of compositing with pseudocapacitance material, so as to improve the specific capacitance of the material. Wang et al.^[11] used the in-situ growth of NiCo₂O₄ nanosheets on CF to obtain a 2D/3D composite material (CF-NiCo₂O₄) with excellent electrochemical properties. In this study, we chose the second way to composite CF with pseudocapacitance materials and obtain higher specific capacitance. There are many considerations in the selection of pseudocapacitance materials. Manganese is abundant in nature, and its oxide has excellent performance in cost, environmental friendliness, high voltage window and theoretical specific capacitance value reaching 1370 F/g^[17–23]. It is widely adopted in the field of supercapacitor electrode materials. However, due to the characteristics of easy agglomeration of manganese oxides in the preparation process and the disadvantage of poor conductivity of manganese oxides, the specific capacitance of manganese oxides is often less than the theoretical value in practical applications. In order to solve these problems, on the one hand, the nanometer material of manganese oxide could be prepared to increase the specific surface area; on the other hand, the composite with carbon material can improve its conductivity. An et al.^[24] and Wang et al.^[25] prepared respective Mn₃O₄/MWCNT and Mn₃O₄/graphene composite material with excellent performance. The specific capacitance of Mn₃O₄/graphene composites in 1 M Na₂SO₄ is 175 F/g, and the specific capacitance in 6 M KOH electrolyte is 256 F/g. Based on this consideration, it would be a good choice to compositing 0D Mn₃O₄ nanoparticles with 3D CF to provide high capacitance.

In this paper, 3D CF was firstly prepared by a carbonization method through MF and used as the growth skeleton, and 0D Mn₃O₄ nanoparticles were then grown on the surface of CF by a one-step hydrothermal method to prepare Mn₃O₄@CF composites with different mass ratios. In order to determine whether the composite was synthesized successfully, many characterization methods were used to analyze the composition and molecular structure, surface Raman scattering signal, valence state, microstructure and its electrochemical performance. The relationship among constituent, microstructure and properties was comprehensively explored. The influence of the structure design in CF and Mn₃O₄ composites on the

electrochemical performance was analyzed. The results show that CF and Mn_3O_4 can play a synergistic role through the structural design, and greatly improve the overall electrochemical performance.

2. Experimental

2.1 Preparation of CF

CF was prepared by a direct carbonization method. MF was cut as $1\text{ cm} \times 2\text{ cm} \times 2\text{ cm}$, and washed with deionized water and ethanol for several times. MF plates were dried in a furnace at $60\text{ }^\circ\text{C}$ for 48 h. The covered alumina crucible and flowing nitrogen were used to carbonize the dry MF with the heating rate of $10\text{ }^\circ\text{C}/\text{min}$. The temperature was firstly kept at $400\text{ }^\circ\text{C}$ for 1 h, and then kept at $800\text{ }^\circ\text{C}$ for 2 h. After naturally cooling to room temperature, CF is obtained.

2.2 Preparation of Mn_3O_4

Mn_3O_4 was prepared by a hydrothermal method. $\text{Mn}(\text{CH}_3\text{COO})_2$ (60 mg) was added into 18 ml anhydrous ethanol, and it was completely dissolved by magnetic stirring for 30 min. The solution was transferred to a high-pressure reactor (25 mL, lined with polytetrafluoroethylene). The hydrothermal reaction was conducted for 3 h at a constant temperature of $150\text{ }^\circ\text{C}$. After the hydrothermal reaction, it was cooled to room temperature naturally, and the samples could be collected by centrifuge. The samples were washed with anhydrous ethanol and deionized water for 3 times, and kept in the drying oven at $60\text{ }^\circ\text{C}$ for 24 h. Finally, Mn_3O_4 monomer was obtained.

2.3 Preparation of $\text{Mn}_3\text{O}_4@\text{CF}$ composites

$\text{Mn}_3\text{O}_4@\text{CF}$ composites were prepared by a one-step hydrothermal method (Fig. 1.). $\text{Mn}(\text{CH}_3\text{COO})_2$ (30 mg) was added into 18 ml anhydrous ethanol, and it was completely dissolved by magnetic stirring for 30 min. The solution containing four pieces of CF were transferred to the high-pressure reactor. The reactor was placed in a constant temperature drying oven, and the hydrothermal reaction was conducted at $150\text{ }^\circ\text{C}$ for 3 h. After the hydrothermal reaction, it was cooled to room temperature. The samples were washed with anhydrous ethanol and deionized water for 3 times, and kept in the drying oven at $60\text{ }^\circ\text{C}$ for 24 h. Finally, $\text{Mn}_3\text{O}_4@\text{CF}$ composite ($\text{Mn}_3\text{O}_4@\text{CF}$ -1) was obtained. In the similar process, $\text{Mn}(\text{CH}_3\text{COO})_2$ with 60 mg and 90 mg was added in, and the obtained materials were denoted as $\text{Mn}_3\text{O}_4@\text{CF}$ -2 and $\text{Mn}_3\text{O}_4@\text{CF}$ -3, respectively.

2.4 Characterization and electrochemical analysis

X-ray diffractometer (Germany Bruker, D8 ADVANCE); laser Raman spectrometer (USA Thermo Fisher, DXR); X-ray photoelectron spectrometer (USA Thermo Fisher, ESCALAB 250Xi); field emission scanning electron microscope (Japan Electronics Corporation, JEOL JSM-7800F); and transmission electron microscope (Japan Electronics Corporation, JEOL JEM-2100) were used to characterize the materials.

We used the electrochemical workstation (Shanghai ChenHua Instrument Co., LTD, CHI 760E) to test the electrochemical performance of the material. The capacitive performance of the material was studied by analyzing the CV curves of the same working electrode at different scanning rates and the CV curves of different working electrodes at the same scanning rates. The specific capacitance and cyclic performance of the material were studied by analyzing the GCD curve of the working electrode under different current density, the GCD curve of different working electrode under constant current density, and the GCD curve of multiple charge-discharge under constant current density. The equivalent circuit diagram of the electrode system was obtained by fitting EIS impedance spectrum, and the kinetic parameters of the electrode system were estimated.

3. Results And Discussion

Figure 2a shows the XRD patterns of CF, Mn_3O_4 and $\text{Mn}_3\text{O}_4@\text{CF}$. The XRD pattern of CF has only two weak broad peaks. The characteristic peaks of Mn_3O_4 are located at 18.2° , 28.8° , 32.5° , 36.5° , 44.4° , 50.8° and 59.9° . These characteristic peaks are corresponded to the (101), (112), (103), (211), (220), (105) and (224) planes of rhodochrome-type Mn_3O_4 (JCPDS No.24-0734)^[26]. The characteristic peaks of $\text{Mn}_3\text{O}_4@\text{CF}$ -2 and $\text{Mn}_3\text{O}_4@\text{CF}$ -3 are obvious at 18.2° , 32.5° and 36.5° , which can prove the existence of Mn_3O_4 in $\text{Mn}_3\text{O}_4@\text{CF}$ -2 and $\text{Mn}_3\text{O}_4@\text{CF}$ -3. The characteristic peaks of Mn_3O_4 are not obviously found due to the less mass of Mn_3O_4 in $\text{Mn}_3\text{O}_4@\text{CF}$ -1.

Since the characteristic peaks of carbon in the XRD diffraction pattern are not obvious, Raman spectral test was conducted on CF and three $\text{Mn}_3\text{O}_4@\text{CF}$ composites to verify the successful synthesis of CF and $\text{Mn}_3\text{O}_4@\text{CF}$ composites. As shown in Fig. 2b, all $\text{Mn}_3\text{O}_4@\text{CF}$ composites have strong peaks at 651 cm^{-1} , which are typical Raman peaks in A_{1g} mode. The tetrahedral vibration of Mn-O bond and the stretching of MnO_6 octahedron lead to this strong peak, which confirms the successful preparation of Mn_3O_4 . The other two characteristic peaks of CF and $\text{Mn}_3\text{O}_4@\text{CF}$ are located at 1352.1 cm^{-1} and 1572.8 cm^{-1} . These two peaks correspond to D peak on the surface of CF caused by incomplete graphite structure microcrystals, structural defects and unsaturated carbon atoms on the surface of CF, and G peak which reflects the degree of crystal structure disorder of carbon materials through relative strength. These two characteristic peaks provide evidence for the successful preparation of CF and $\text{Mn}_3\text{O}_4@\text{CF}$ composites.

XPS analysis was carried out on the surface of $\text{Mn}_3\text{O}_4@\text{CF}$ -2. As shown in Fig. 3, the XPS spectrum of each element and the XPS full spectrum (Fig. 3a) of $\text{Mn}_3\text{O}_4@\text{CF}$ -2 were obtained respectively. Through the spectrum, the composition and atoms of elements on the material surface especially the chemical states of N and Mn elements could be further determined. The surface elements of the composite can be identified as C, N, O and Mn in the full spectrum. Figure 3b is the narrow spectrum of element C. Peak fitting analysis of this spectrum shows that when the binding energy is 284.3 eV , there is a strong characteristic peak corresponding to the C-C and C = C bonds hybridized by sp^2 in CF. This indicates that C atoms in CF are mostly connected in the form of covalent bonds to eliminate the original interface

resistance among microstructure units, provide carrier channels that can be transported in a long range, and improve the conductivity of the material greatly. The peaks corresponding to the C-C and O = C-O bonds are located at the binding energies of 286.6 eV and 288.0 eV, respectively. It can be seen that a large number of oxygen-containing functional groups existing on the surface of CF. During the hydrothermal reaction, these oxygen-containing functional groups would be the nucleation sites of Mn_3O_4 and combine CF and Mn_3O_4 in the form of covalent bonds. In addition, there is a peak at 285.8 eV corresponding to the C-N bond in the C 1 s spectrum and indicating that part of the N elements in CF are combined in the form of covalent bonds. Thus, the CF prepared by MF carbonization is a N-doped C material. As shown in Fig. 3c, the existence state of N element in CF is further analyzed by performing peak fitting analysis. There are three main forms of N element in CF. One is the graphitized N element, corresponding to the binding energy of 389.9 eV. The second is pyrrole N, corresponding to the binding energy of 400.0 eV. The third is pyridine N, corresponding to the binding energy of 403.4 eV. N-doping is very favorable for electron transport during redox reaction^[27]. As shown in Fig. 3d, the peak fitting analysis of O elements shows that there are three characteristic peaks corresponding to the Mn-O-Mn, Mn-O-H and O = C-O bond at the respective binding energies of 529.2 eV, 531.2 eV and 532.8 eV, indicating that $\text{Mn}_3\text{O}_4@\text{CF}-2$ was successfully prepared. In particular, the existence of Mn-O-H bond proves that Mn_3O_4 has a strong interaction with CF^[28]. As shown in Fig. 3e, it verifies the chemical state of Mn in $\text{Mn}_3\text{O}_4@\text{CF}-2$. There are two sharp peaks at the binding energy of 641.2 eV and 652.8 eV corresponding to Mn 2p_{3/2} and Mn 2p_{1/2}, respectively. The splitting energy between the two peaks is 11.6 eV, which is consistent with Mn_3O_4 in the previous report^[29]. By analyzing the XPS spectrum of $\text{Mn}_3\text{O}_4@\text{CF}-2$, it is proven that $\text{Mn}_3\text{O}_4@\text{CF}-2$ was successfully synthesized and CF was the N-doped carbon material.

Figure 4a-b are the scanning images of CF, which clearly show that a very uniform 3D skeleton in CF consists of a large number of interconnected fibers with a diameter of about 5 μm connected to each other by nodes. Figure 4c-d are the scanning images of Mn_3O_4 monomer. Mn_3O_4 is a ball with a diameter of about 12 μm , which is formed by the agglomeration growth of Mn_3O_4 nanoparticles.

As shown in Fig. 5, $\text{Mn}_3\text{O}_4@\text{CF}$ composites with different contents were characterized by SEM. The figures clearly show that the surfaces of $\text{Mn}_3\text{O}_4@\text{CF}$ composites are different from the smooth CF. There are Mn_3O_4 nanoparticles loaded on CF surfaces. When $\text{Mn}(\text{CH}_3\text{COO})_2$ (30 mg) was added during the hydrothermal reaction, only a small number of Mn_3O_4 nanoparticles are grown on the surface of CF (Fig. 5a-d). When the mass of $\text{Mn}(\text{CH}_3\text{COO})_2$ was 60 mg, a large number of Mn_3O_4 nanoparticles are grown uniformly on the surface of CF (Fig. 5b-e). Different from Mn_3O_4 monomer, Mn_3O_4 nanoparticles in $\text{Mn}_3\text{O}_4@\text{CF}-2$ are not agglomerated during the growth process. When the mass of $\text{Mn}(\text{CH}_3\text{COO})_2$ was 90 mg, the surface of CF is completely covered by a large number of Mn_3O_4 nanoparticles, and the nanoparticles agglomerated like Mn_3O_4 monomer (Fig. 5e-f). Through the above analysis, it can be found that CF is feasible and effective to be applied as the growth framework to avoid the agglomeration of Mn_3O_4 nanoparticles. The appropriate technique can evenly disperse nanoparticles. There are abundant spaces among particles, which is beneficial for increasing more active sites and ion diffusion of

electrolyte in the Faraday redox reaction, effectively improving the electric capacity in the process of charging and discharging.

In order to determine the size of the prepared Mn_3O_4 nanoparticles, ultrasonic oscillations were used to treat $\text{Mn}_3\text{O}_4@\text{CF}-2$, and Mn_3O_4 nanoparticles were obtained. Then, the Mn_3O_4 nanoparticles were observed by TEM (Fig. 6). It can be seen that $\text{Mn}_3\text{O}_4@\text{CF}-2$ contains very uniform Mn_3O_4 nanoparticles with the size of 18 nm, which could improve the electrochemical performance.

The EDX energy spectra of $\text{Mn}_3\text{O}_4@\text{CF}-2$ were obtained to analyze the element type and the distribution of each element (Fig. 7). It can be confirmed that the elements of $\text{Mn}_3\text{O}_4@\text{CF}-2$ are C, N, O and Mn. These elements are uniformly distributed on the CF skeleton, which strongly supports the above analysis results of XRD, Raman and XPS, and further confirms that CF and Mn_3O_4 constitute the composite.

The GCD curve of CF at different current densities, presenting a symmetrical triangle (Fig. 8a). Figure 8b shows the CV curve of CF at different scanning rates, whose curve shape is approximately rectangular. It can be seen that CF has good characteristics of EDLC capacitance. Figure 8c shows the GCD curve of Mn_3O_4 monomer at different current densities, and Fig. 8d shows the CV curve of Mn_3O_4 at different scanning rates. Different from CF, Mn_3O_4 monomer has a platform in the process of charging and discharging on the curve of GCD, while it also has a redox peak on the curve of CV. It proves that Mn_3O_4 monomer has excellent pseudo-capacitance characteristics.

Figure 9a shows the GCD curves of $\text{Mn}_3\text{O}_4@\text{CF}-2$ at different current densities, and Fig. 9b shows the CV curves of $\text{Mn}_3\text{O}_4@\text{CF}-2$ at different scanning rates. As shown in Fig. 9a, due to the introduction of Mn_3O_4 nanoparticles, the pseudocapacitance is increased. The charge-discharge curve of $\text{Mn}_3\text{O}_4@\text{CF}-2$ shows asymmetry. As shown in Fig. 9b, there is an obvious redox peak on the CV curve of $\text{Mn}_3\text{O}_4@\text{CF}-2$. By comparison with Mn_3O_4 monomer, it can be found that the redox peak of $\text{Mn}_3\text{O}_4@\text{CF}-2$ is gradually obvious with the increase of the scanning rate, and has a certain deviation. However, the redox peak of Mn_3O_4 monomer became less obvious with the increase of the scanning rate. This difference indicates that $\text{Mn}_3\text{O}_4@\text{CF}-2$ has better rate capability than Mn_3O_4 monomer.

As shown in Fig. 9c-d, GCD and CV tests were performed on CF, $\text{Mn}_3\text{O}_4@\text{CF}-1$, $\text{Mn}_3\text{O}_4@\text{CF}-2$ and $\text{Mn}_3\text{O}_4@\text{CF}-3$ at 1 A/g current density and 100 mV/s scanning rate, respectively. As shown in Fig. 9c, the charging and discharging time of $\text{Mn}_3\text{O}_4@\text{CF}-2$ is the longest at 1 A/g current density, therefore, the specific capacitance of $\text{Mn}_3\text{O}_4@\text{CF}-2$ is the highest among the four test samples. Different from the GCD curve of CF, the GCD curve of $\text{Mn}_3\text{O}_4@\text{CF}$ is asymmetric, which indicates that the specific capacitance of $\text{Mn}_3\text{O}_4@\text{CF}$ is enhanced by the additional pseudo-capacitance provided by Mn_3O_4 nanoparticles. As seen from Fig. 9d, the CV curve of CF is similar to a rectangle, and there are obvious redox peaks on the CV curves of $\text{Mn}_3\text{O}_4@\text{CF}$. Therefore, the capacitor of CF is mainly provided by EDLC, while the capacitor of $\text{Mn}_3\text{O}_4@\text{CF}$ composite material is provided by both EDLC and pseudocapacitance.

Figure 10a is a schematic diagram of the electron transmission of $\text{Mn}_3\text{O}_4@\text{CF}-2$. The reasons for the composite with the capacitance increase are two aspects. On the one hand, 3D CF serves as the skeleton for growth. The uniform load of Mn_3O_4 nanoparticles on CF greatly increases its contact area with the electrolyte and the number of active sites, providing a high additional pseudo-capacitance for the electrode material. On the other hand, the specific surface area of the composite increases due to the special morphology of Mn_3O_4 nanoparticles. The rapid channel of electrolyte ion migration is retained, thus reducing the diffusion resistance of electrolyte ions between the electrolyte and the electrode material. In addition, CF as the conductive skeleton of the composite can also enhance the overall conductivity. As shown in Fig. 10b, the GCD curves of CF, Mn_3O_4 and $\text{Mn}_3\text{O}_4@\text{CF}-2$ at different current densities are calculated, and the specific capacitance at different current densities can be obtained. The specific capacitance of CF from 1 A/g to 5 A/g is calculated, and the results are 79.1, 69.8, 63.9, 61.5 and 59.4 F/g. Similarly, the specific capacitance of Mn_3O_4 from 1 A/g to 5 A/g is calculated to be 112.7, 81.6, 73.1, 62.3 and 54.8 F/g. The specific capacitance of $\text{Mn}_3\text{O}_4@\text{CF}-2$ from 1 A/g to 5 A/g is 212.8, 178.1, 164.3, 150 and 142.9 F/g respectively. As the contact area between the uniformly loaded Mn_3O_4 nanoparticles and the electrolyte is greatly increased, the number of active sites is increased, and a very high pseudo-capacitance is contributed to the electrode material. Therefore, compared with those of CF and Mn_3O_4 monomers, the specific capacitance of $\text{Mn}_3\text{O}_4@\text{CF}-2$ is greatly improved. Figure 10c shows the specific capacity change of $\text{Mn}_3\text{O}_4@\text{CF}-2$ at 1 A/g current density for 2000 cycles. After 2000 cycles, $\text{Mn}_3\text{O}_4@\text{CF}-2$ can still maintain the initial specific capacitance of 86.1%, which shows that $\text{Mn}_3\text{O}_4@\text{CF}-2$ has good cycling performance.

As shown in Fig. 10d, Nyquist plots were obtained by conducting EIS tests on CF, Mn_3O_4 and $\text{Mn}_3\text{O}_4@\text{CF}-2$ at frequencies ranging from 0.1 Hz to 100 kHz. The Nyquist plot is divided into two parts, namely a semicircle at high frequencies and an oblique line at low frequencies. The equivalent series resistance (R_s) on the Nyquist curve is represented as in Z' axial intercept. The charge transfer resistance (R_{ct}) resulting from the transfer of electrons between the electrolyte and the electrode material in an electrochemical reaction is expressed as the radius of the circle in the high frequency region. The diffusion resistance (R_w) is expressed as the slope of the oblique line in the low-frequency region, and the diffusion resistance between the electrolyte ions existing in the electrolyte and the electrode material. The R_s of CF, Mn_3O_4 and $\text{Mn}_3\text{O}_4@\text{CF}-2$ are 1.3, 2.1 and 1.6 Ω , respectively. It can be seen that the equivalent series resistance of the composite is greatly reduced by using CF as the conductive skeleton. The R_{ct} of CF, Mn_3O_4 and $\text{Mn}_3\text{O}_4@\text{CF}-2$ are 0.5, 3.6 and 0.6 Ω , respectively. It confirms that the electron transport efficiency between the electrolyte and the electrode material is improved by CF as the conductive skeleton. Compared with that of Mn_3O_4 , the oblique slope of CF and $\text{Mn}_3\text{O}_4@\text{CF}-2$ are larger in the low frequency region. The maximum oblique slope of $\text{Mn}_3\text{O}_4@\text{CF}-2$ is in the low frequency region, which has a smaller diffusion resistance of electrolyte ions. According to the AC impedance analysis, CF can greatly improve the conductivity of Mn_3O_4 . Through the synergistic action of CF and Mn_3O_4 nanoparticles, $\text{Mn}_3\text{O}_4@\text{CF}-2$ shows extremely high electrochemical performance.

4. Conclusions

In this study, $\text{Mn}_3\text{O}_4@\text{CF}$ with 0D@3D structure was prepared by Mn_3O_4 nanoparticles grown on the foam carbon (CF) skeleton. A series of methods were used to study the electrochemical properties of CF, Mn_3O_4 monomer and $\text{Mn}_3\text{O}_4@\text{CF}$. The results show that using CF as the growth framework can effectively prevent the agglomeration of Mn_3O_4 nanoparticles, which are 18 nm in diameter and uniformly distributed on the $\text{Mn}_3\text{O}_4@\text{CF}$ -2. Through electrochemical testing of CF and Mn_3O_4 , it is found that CF has good EDLC capacitance characteristics and Mn_3O_4 has excellent pseudocapacitance characteristics. It is found that the specific capacitance of the composite was significantly higher than that of CF and Mn_3O_4 . The specific capacitance of $\text{Mn}_3\text{O}_4@\text{CF}$ -2 is the largest at the current density of 1 A/g, reaching 212.8 F/g. CF as the skeleton can improve the conductivity of the composite, which greatly improves the electrochemical performance. There are two reasons for this improvement in electrochemical performance. First, 3D CF is used as the growing matrix to prevent the agglomeration of Mn_3O_4 nanoparticles. Mn_3O_4 nanoparticles are uniformly loaded on CF, which greatly increase the contact area and active sites with the electrolyte, and provide high pseudocapacitance for the electrode material. Second, using CF as the conductive skeleton can effectively improve the overall conductivity of the composite. The results prove the possible application of $\text{Mn}_3\text{O}_4@\text{CF}$ for supercapacitor. It should be explored more real application in supercapacitor devices.

Declarations

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Figures

Figure 1

Schematic illustration of the synthesis for Mn₃O₄@CF.

Figure 2

(a) XRD patterns of CF, Mn_3O_4 and $\text{Mn}_3\text{O}_4@\text{CF}$; (b) Raman patterns of CF and $\text{Mn}_3\text{O}_4@\text{CF}$.

Figure 3

(a) XPS full survey spectrum of Mn₃O₄@CF-2 composite and corresponding XPS profiles of (b) C 1s, (c) N 1s, (d) O 1s and (e) Mn 2p.

Figure 4

SEM images of (a-b) CF, (c-d) Mn_3O_4 .

Figure 5

SEM images of (a, d) $\text{Mn}_3\text{O}_4@\text{CF}-1$, (b, e) $\text{Mn}_3\text{O}_4@\text{CF}-2$, (c, f) $\text{Mn}_3\text{O}_4@\text{CF}-3$.

Figure 6

TEM images of (a-b) $\text{Mn}_3\text{O}_4@\text{CF}-2$.

Figure 7

EDX images of Mn₃O₄@CF-2.

Figure 8

GCD curves at different current density of (a) CF, (c) Mn₃O₄; CV curves at different scan rate of (b) CF, (d) Mn₃O₄.

Figure 9

(a) GCD curves at different current density of $\text{Mn}_3\text{O}_4@\text{CF}-2$; (b) CV curves at different scan rate of $\text{Mn}_3\text{O}_4@\text{CF}-2$; (c) GCD curves at 1 A/g of CF and $\text{Mn}_3\text{O}_4@\text{CF}$; (d) CV curves at 100 mV/s of CF and $\text{Mn}_3\text{O}_4@\text{CF}$.

Figure 10

(a) Schematic diagram of Mn₃O₄@CF-2 electron transfer process; (b) The specific capacitances of CF, Mn₃O₄ and Mn₃O₄@CF-2 at different current densities; (c) Cycling performance of Mn₃O₄@CF-2 at a current density of 1 A/g; (d) Nyquist plots of CF, Mn₃O₄ and Mn₃O₄@CF-2.