X PREPARATION AND CHARACTERIZATION OF CARBON-BASED COMPOSITE NANOFIBERS FOR SUPERCAPACITOR

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Abstract:

Polyacrylonitrile (PAN)/Co(OAc)₂/carbon nanotubes (CNTs) composite nanofibers were fabricated via electrospinning with N,N-dimethylformamide (DMF) as solvent, and by carbonization and activation of the above precursor nanofibers, porous carbon composite nanofibers were successfully obtained. Scanning electron microscope, X-ray diffraction, ASAP 2020, and Solartron 1470 were used to characterize the surface morphology, the phase composition, specific surface area, and electrochemical property of the nanofibers, respectively. The result showed that some of the fibers were broken after sintering, and the surface area and pore volume of the porous C/Cu/CNTs were 771 m²/g and 0.347 cm³/g, respectively. The specific capacitance of the composite nanofibers reached up to 210 F/g at the current density of 1.0 A/g. Its energy density and power density were 3.1 Wh/Kg and 2,337 W/Kg, respectively, at the current of 0.5 and 5 mA.

Keywords:

electrospinning; carbon nanotube; nanofiber; electrochemical property; specific capacitance

1 Introduction

Chemical double-layer capacitor, also known as supercapacitor, is a new kind of energy storage device between static capacitor and traditional chemical power source. With the speedness of charging and discharging, high efficiency as well as long cycle life, it's widely used in portable electronic devices and cars [1-2]. Porous carbon composites became one of the most commonly used electrode materials because of its good conductivity, electrochemical stability, and low cost [3]. Supercapacitor stores electricity by physically absorbing electrolyte ions to the surface of porous carbon electrode. Therefore, specific surface areas, pore size distributions, and electrical conductivity are key factors affecting the storage capacity of porous materials [4]. It's capacitance is not proportional to specific surface areas, so pore size distributions and electrical conductivity of the material need to be improved as well as specific surface areas of electrode materials in order to improve its electrochemical performances [5]. Porous materials are widely used in catalyst carriers, sensors, electronic materials, filter materials, and energy storage materials and, therefore, have become a research hotspot.

Electrospinning is a technology to prepare top-down continuous micro- or nanofibers. Compared with traditional preparation methods of nanofibers such as chemical vapor deposition, laser vaporization, arc discharge, and template method, it's environmentally friendly and has advantages of simpler technique and higher efficiency. Meanwhile, electrospinning nanofibers have controllable diameters and bigger specific surface areas [6-7]. Carbon nanofibers treated in high temperatures have a better electrical conductivity and can be directly used as supercapacitor electrode materials without adding any conductive agent or adhesive [8-9].

Response surface methodology (RSM) is statistical methods using multiple quadratic regression equations to fit the function between factors and response values in order to solve multivariate problems [10-13], in which the method of second-order Box-Behnken designing (BBD) based on three levels needs less test data and has a higher efficiency, with experimental factors not in extreme levels simultaneously and all experimental points located in safe operation regions. So far, this method has been more widely used in optimizations of biomedicine [14], chemical synthesis procedure [15], food fermentation [16], and so on.

In recent years, using electrospinning polymer fibers, matrix of carbon fibers has gained more and more attention. Using polyacrylonitrile (PAN)/polyvinyl pyrrolidone (PVP)/Cu(OAc)₂ and N,N-dimethylformamide (DMF) as precursor and solvent, respectively, porous carbon composite nanofibers were obtained at different ratios adopting electrospinning and high-temperature carbonization. Researches on its electrochemical capacitance performance were conducted, and the effects of different ratios on capacitance were systematically studied. As a result, its proportional parameters were optimized.

2 Experiments

2.1 Materials and equipments

PAN, molecular weight of 100,000, the United States Faith-Group Co., Ltd; PVP, Sinopharm Chemical Reagent Co., Ltd; copper acetate (Cu(OAc)₂), Sinopharm Chemical Reagent Co., Ltd; DMF, Sinopharm Chemical Reagent Co., Ltd; carbon nanotubes (CNTs), Chengdu Institute of Organic Chemistry,

Chinese Academy of Sciences; Homemade electrospinning equipments; S-4800 Scanning Electron Microscope; Rigaku Micromax-002 X-ray Diffractometer (R-Axis IV++); ASAP 2020 Adsorption Instrument.

2.2 Preparation of precursor solution

A certain amount of CNTs were weighed and added to DMF solution and then vibrated for 8 hours in ultrasonic vibration generator till transparent homogeneous solution was formed. Then prepared PAN was added to aforementioned solution and stirred sufficiently for 2 hours. Lastly, $\text{Cu}(\text{OAc})_2$ was added to PAN/CNTs solution and stirred sequentially for 2 hours, after which PAN/PVP/ $\text{Cu}(\text{OAc})_2$ composite nanofiber solvent was prepared as electrospinning solvent. The mass fraction of its solute was 10%, and PAN occupied 90% of the content, while the mass fraction of CNTs was 0.5%.

2.3 Preparation of PAN/PVP/ $\text{Cu}(\text{OAc})_2$ composite nanofibers

Prepared spinning solution was poured into an injector with the capacity of 20 mL and the needle diameter of 0.5 mm. During electrospinning procedure, a voltage of 15 kV was applied to the needle, and the aluminum foil as a receiver was connected to earth. The needle and aluminum foil had a distance of 15 cm, and the injection pump had a flux of 0.5 mL/h. Nanofibers collected from the aluminum foil was then prepared after drying. PAN/ $\text{Cu}(\text{OAc})_2$ composite nanofibers were also prepared for the purpose of comparison afterwards.

2.4 Preparation of C/Cu/CNTs composite nanofibers

Aforementioned precursor composite nanofibers were put into a box furnace, and detailed steps are as follows: first, heating the nanofibers to 250 °C at a rate of 2 °C/min in air and keeping the temperature for 4 hours with an air flow rate of 20 PSI; second, under the protection of nitrogen, continuing heating up to 800 °C at a rate of 5 °C/min and keeping the temperature for 6 hours with a nitrogen flow of 20 PSI; Third, stopping pumping in nitrogen and switching to CO_2 with a flow of 20 PSI, kept for 30 min under the temperature of 800 °C; Fourth, switching CO_2 to nitrogen with a flow of 20 PSI till the temperature of the box furnace was cooled down to room temperature, after which the sample was prepared finally.

2.5 Test of electrochemical performance

The test of electrochemical performance adopted a double-electrode system and was conducted using Solartron 1470 in Solartron Analytical, Houston, TX, with a electrode diameter of 1.25 cm. KOH solvent with a mole fraction of 6.0 mol/L was adopted.

3 Results and discussion

3.1 Box—Behnken designing and analysis

Based on response values in Table 1 from the 17 experiments designed by Box and Behnken, the quadratic regression fitting was carried out and a quadratic equation with interaction

items and quadratic terms was obtained. The main effects and interaction effects of various factors were analyzed, and the optimum value was obtained in a certain level. Significance tests of the regression equation were shown in Table 2.

Table 1. Results of experimental design by RSM

Numbers	Codes			C_{sp} (F/g)
	X	Y	Z	
1	0	0	0	99
2	0	0	0	83
3	1	0	1	54
4	0	0	0	98
5	0	-1	1	50
6	1	0	-1	81
7	-1	0	1	57
8	1	-1	0	88
9	0	1	1	55
10	-1	0	-1	84
11	-1	-1	0	93
12	-1	1	0	95
13	0	-1	-1	57
14	0	0	0	96
15	0	0	0	98
16	0	1	-1	74
17	1	1	0	86

Table 2. Analysis of variance value of regression equation

	Coefficient Estimates	Standard Deviation	Values of F	Values of P
Intercepts	94.80	3.14		
X	-2.50	2.48	1.01	0.3476
Y	2.75	2.48	1.23	0.3047
Z	-10.00	2.48	16.22	0.0050
XY	-1.00	3.51	0.081	0.7841
XZ	0.000	3.51	0.000	1.0000
YZ	-3.00	3.51	0.73	0.4212
X^2	2.85	3.42	0.69	0.4325
Y^2	-7.15	3.42	4.36	0.0751

Quadratic multiple regression model obtained from regression analysis was as follows: $C_{sp} = 94.8 - 2.50X + 2.75Y - 10.0Z - 1.0XY - 3.0YZ + 2.85X^2 - 7.15Y^2 - 28.65Z^2$

It can be seen from Table 2 that the value of R^2 in regression equation is equal to 0.93. And it showed that this equation has a better fitting degree and can be used for the prediction of

capacitance. In the equation, P values of both Z and Z^2 are less than 0.05, which means that the mass fraction of $\text{Cu}(\text{OAc})_2$ and its quadratic term have a significant influence on capacitance. The optimal ratio of PAN, PVP, and $\text{Cu}(\text{OAc})_2$ is 76:14:10. Simultaneously, the sample has a capacitance of 95.8 F/g and has a difference ratio of 5.2% with predicted values, which shows that this model is effective in a certain range.

It can be directly known from Figure 1 that the content of PAN, PVP, and $\text{Cu}(\text{OAc})_2$ is not the higher and the better. The response curves of PVP and $\text{Cu}(\text{OAc})_2$ are a little steep, which means that interaction between PVP and $\text{Cu}(\text{OAc})_2$ is outstanding while interaction between PAN and PVP is unremarkable, and PVP has no interaction with $\text{Cu}(\text{OAc})_2$.

Figure 1. Contour plots showing the effects of the factors on response. (a) PAN and PVP concentration; (b) PAN and $\text{Cu}(\text{OAc})_2$ concentration; (c) PVP and $\text{Cu}(\text{OAc})_2$ concentration

3.2 X ray-diffraction analysis

Figure 2. XRD patterns of carbon-based composite nanofibers

X-ray diffraction (XRD) patterns of PAN/ $\text{Cu}(\text{OAc})_2$ /CNTs precursor composite nanofibers after high-temperature calcination are shown in Figure 2. It can be seen that there exists a wide peak at $2\theta = 25^\circ$ because of partial crystallization of carbon fibers, corresponding to crystal 002 (JCPDS 70-1478). Other two diffraction peaks are corresponded to pure copper 111 and crystal 200 (JCPDS 15-0806) with $2\theta = 44.2^\circ$ and $2\theta = 51.5^\circ$, respectively. According to Scherrer equation, the average grain size that is perpendicular to the crystal 111 is 16.8 nm.

3.3 Scanning electron microscope analysis

It can be observed from Figure 3(a) that surfaces of precursor PAN/ $\text{Cu}(\text{OAc})_2$ /CNTs composite nanofibers are relatively smooth, while surfaces of partial fibers are still rugged, which is due to relatively even entanglement of PAN macromolecules dissolving in DMF. When spinning jet flow is speeding up in the electric field, PAN macromolecules stretch and align along the fiber's length. Molecular weight of $\text{Cu}(\text{OAc})_2$ in the surface of spinning jet flow is smaller, so that molecules move faster, while PAN molecules move slowly. With the volatilization of DMF, spots where molecules move fast dent while spots where molecules move slowly swell naturally.

As shown in Figure 3(b), diameters of C/ Cu /CNTs composite nanofibers are thinner and brittle fracture occurs in partial fibers after high-temperature calcination. This is because PAN and $\text{Cu}(\text{OAc})_2$ discompose under high temperature and volatilize as gases during pre-oxidization and carbonization, and simultaneously, fiber weight decreases when carbon in composite nanofibers reacts with activator CO_2 during activation stage. Besides, when calcined under high temperature, precursor composite nanofiber PAN/ $\text{Cu}(\text{OAc})_2$ /CNTs brittly breaks at its weak links.

3.4 N_2 adsorption-desorption curves and pore size distribution plot

It can be seen from Figure 4 that N_2 isothermal absorption-desorption curve of C/ Cu /CNTs carbon composite nanofibers belongs to type I (IUPAC) and has a typical microporous

(a)

(b)

Figure 3. Scanning electron microscopic images of carbon composite nanofiber

Figure 4. N₂ adsorption-desorption isotherm and pore distribution plot (insert)

structure^[20]. It can be observed from pore size distribution plot that pore sizes of C/Cu/CNTs composite nanofibers distribute narrowly, mainly between 0 and 2.0 nm.

Data related to specific surface area and pore volume of samples are shown in Table 3. It shows that the specific surface area and pore volume of C/Cu/CNTs composite nanofiber are 771 m²/g and 0.347 cm³/g, respectively, and increase by 53% and 35%, respectively, compared with C/Cu composite nanofibers. In addition, micropore, mesopore, and macropore coexist in nanofiber pores, in which micropore occupies the largest proportion in pores, that is, 79% and 92%, respectively.

Table 3. Surface area and pore volume of carbon composite nanofiber

Samples	Specific surface areas (m ² /g)	Pore volumes (cm ³ /g)			
		Micropore	Mesoporous	Macropore	Total volume
C/Cu	503	0.204	0.044	0.009	0.257
C/Cu/CNTs	771	0.319	0.022	0.006	0.347

3.5 Electrochemical performance analysis

Cyclic voltammetry (CV) and galvanostatic charge-discharge were used to study electrochemical performance of C/Cu/CNTs composite nanofibers. Galvanostatic charge-discharge tests were carried out in the voltage range of 0–0.8 V, with electric currents of 0.5, 1.0, 3.0, and 5.0 mA. Scanning speeds are set at 3, 5, and 10 mV/s when carrying out CV tests.

3.5.1 Cyclic voltammetry tests

Figure 5. Cyclic voltammograms of carbon nanofibers

It can be seen from Figure 5 that cyclic voltammograms of samples approximate rectangles without reduction and oxidation peak, showing that this electrode material acts as

capacitance almost totally because of its electrochemical double-layer capacitor. The shape of cyclic voltammetry curve had no obvious change with speeding up of scanning, indicating that composite nanofibers have a good capacity retention ratio and are suitable for electrode materials of supercapacitors.

3.5.2 Galvanostatic charge-discharge tests

Figure 6. Charge-discharge curves of carbon nanofibers

As shown in Figure 6, charge-discharge time gets shorter with current increasing. This is because it takes long for electrolyte ions to get into fiber pores to form double-layer capacitance. When current density increases, it needs shorter time to form double layers and capacitance becomes smaller with electrolyte ions hindered. As charge-discharge current increases from 0.5 to 5.0 mA, the discharge curve has no obvious potential drop in internal resistance, which means that this electrode material has good charge-discharge performances and has slight resistance to the spread of electrolyte ions.

3.5.3 Effects of current density on specific capacitance

Figure 7. Specific capacitance as a function of current density

Figure 7 shows the specific capacitance curve as a function of current density. It can be seen that sample curves have good linear relationships under different current densities, which means that this electrode material has very good capacitance performance. When value of current density is 1.0 A/g, sample has a specific capacitance of 210 F/g, having increased about

21% compared with C/Cu composite nanofibers. C/Cu/CNTs composite nanofibers have larger specific surface areas and pore volumes to store more energies. Besides, the addition of CNTs forms a bridge structure between Cu particles, further improving its electrical conductivity as well as its electrochemical properties.

3.5.4 Effects of electric current on power density and energy density

Figure 8. Ragone plots of carbon composite nanofibers

Figure 8 shows Ragone plots of carbon composite nanofibers. It can be seen that energy density of C/Cu/CNTs carbon composite nanofibers decreases as charge-discharge current increases. Its energy density and power density decreases from 3.1 to 2.7 Wh/Kg and increases from 256 to 2,337 W/Kg, respectively, when charge-discharge current increases from 0.5 to 5.0 mA.

4 Conclusion

PAN/Cu(OAc)₂/CNTs composite nanofibers were prepared by electrospinning, and after treated under high temperatures, porous C/Cu/CNTs composite nanofibers were obtained. This kind of carbon composite nanofibers have higher specific surface areas, higher pore volumes, and narrower fiber pore size distributions. It can be used as electrode materials of supercapacitance without any conductive agent or adhesive agent. CNTs play a role of bridge between Cu particles and can improve its electrochemical properties by improving its electrical conductivity. Specific capacity of carbon composite nanofibers reaches 210 F/g when the value of current density is 1.0 A/g.

Through response surface methodology, quadratic multiple regression models of PAN, PVP, and Cu(OAc)₂ with different mass fractions to carbon composite nanofibers' capacitance were obtained. Cu(OAc)₂ has the most significant effect, and secondly quadratic terms of Cu(OAc)₂. Predicted values of the model have a good fitting with practical values. After treated under high temperatures, morphology of fibers become rough and fractures occur in partial fibers. XRD results show that components of optimized carbon composite nanofibers are C/Cu/CuO/Cu₂O.

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