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Study on Preparation of Nanocarbon Fibers from Wheat-Straw Based on Electrostatic Spinning Method and its Application in Supercapacitor

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Wheat-straw carbon nanofiber electrode materials are prepared by means of electrospinning with waste wheat-straw, polyacrylonitrile(PAN) and N,N-dimethylformamide (DMF) as raw materials. After wheat-straw carbon nanofiber precursor is activated with potassium hydroxide, pre-oxidized and carbonizied, different mass ratios of polyacrylonitrile/wheat-straw carbon composition nanofiber electrode materials are obtained. The composition nanofibers with 10% wheat-straw carbon shows excellent electrochemical properties with high specific capacitance of 249.0 F/g at current density is 0.4 A/g and superior cycling stability, remaining a capacitance retention of 96.4% after 1000 cycles at the current density of 2A/g.

Keywords: Electrospinning method; wheat-straw; carbon nanofibers; electrochemical properties; specific capacitance

1. INTRODUCTION

Electrochemical capacitors (ECs) , also called supercapacitors，have higher energy density than conventional dielectric capacitors and much higher power density than rechargeable batteries.[1] Supercapacitor, the function of which ranges between that of common capacitor and chemical batteries is a brand-new energy storage device. It is considered to be the most appropriate clean energy of environment friendly and sustainable development [2]. ECs, especially asymmetric supercapacitors, with dual functions of the electrical double-layer (EDL) capacitor and the pseudocapacitive capacitor, have drawn much attention because of the broad working voltage window，improved energy density and high cycle stability [4-7].

Electrode materials are the main factors that determine the performance of the supercapacitor, so the research on the electrode materials has been focus on the field for many years. Carbon materials have been widely used for making supercapacitor electrode because of the versatile forms(e.g. fibers，tubes，felts，and powers)，reasonable conductivity and excellent stability[7-12]. Its low cost also has promised wide commercial applications.

Electrospinning has been proven to be a useful and convenient strategy for producing nanofibers that can form a three-dimensional network and are desirable for application as energy storage material[13–16]. Indeed, electrospinning is advantageous in making polymer nanofibers with controlled fiber diameter，fiber alignment，and shape of the fibrous mat.[17] In recent years, due to the shortage of fossil resources, the development and application of carbon materials have been limited. Biomass materials, such as forest biomass, agricultural and sideline products, animal manure etc. because of their rich carbon-rich properties, have been used to replace fossil resources, and widely concerned by the researchers [18,19]. Carbon production using waste biomass as raw material can not only reduce production cost but also solve the environmental pollution caused by the direct burning and improper dumping of waste biomass. Biomass carbon nanofibers have the basic physical and chemical properties of carbon materials, such as heat resistance, good chemical inertia, high conductivity and high thermal conductivity. Besides, a large amount of -OH and -COOH and other oxygen functional groups on the biomass carbon surface make them appropriate as supercapacitor electrode materials in a certain extent.

In this study, we develop a convenient and green method to prepare biomass nanofibers using a simple method. At first wheat-straw was pretreated using concentrated sulfuric acid and hydrogen peroxide for the carbonization, and then the treated wheat straw and polyacrylonitrile(PAN) were dispersed in N,N-dimethylformamide(DMF) for spinning. This processing method not only effectively prevents release a mass of toxic and harmful gases, but also significantly improve the final products' performance.

2. EXPERIMENTAL

2.1 Instruments and reagents

2.1. 1 Instruments

The electrospinning apparatus (Yongkang Leye Science and Technology Development Co., Ltd., Beijing.); GSL-1600X tube furnace (Hefei Kejing Materials Technology Co., Ltd., Hefei); Nicolet NEXUS 670 Fourier transform infrared spectrometer(USA); JSM-6701F cold field emission scanning electron microscope(JOEL Japan); CHI660E electrochemical workstation with a platinum electrode as the counter electrode and a saturated calomel electrode as reference electrode(Shanghai Chenhua Instrument Co., Ltd., Shanghai); TG209F1thermal analyzer (Netzsch, Germany).

2.1.2 Reagents

Polyacrylonitrile(PAN, M_w=150,000), was purchased from Macklin, Shanghai, China; N,N-dimethylformamide was obtained from Tianjin Kaitong Chemical Co., Ltd., Tianjing, China;

Concentrated sulfuric acid, hydrogen peroxide, potassium hydroxide were acquired from Tianjin BASF Chemical Co., Ltd., Tianjing, China; Nickel foam was bought from Kunshan Tengerhui Electronic Technology Co., Ltd., Kunshan, China; Conductive graphite, acetylene black were purchased from Tianjin Best Union Chemical Technology Co., Ltd., Tianjing, China; Teflon was obtained from Guangzhou Songbai Chemical Industry Co., Ltd., Guangzhou, China.

2.2. Experimental method

2.2.1 Pretreatment of wheat-straw

Take a certain amount of wheat-straw, crush and clean with distilled water for 2 times, then dry in 80℃ blast drying oven. Weigh accurately processed wheat-straw 30.0002 g into a 500mL beaker, then add 200 mL concentrated sulfuric acid slowly and stir for 20 to 30 minutes, at last add 67 mL H_2O_2 in about 3 hours, under stirring to prevent liquid splashing. The wheat-straw is fully carbonized. Wash the carbonized wheat-straw several times with distilled water under room temperature. The mixture is centrifugally separated when cleaning solution is close to neutral and the filter cake is dried at 80 ℃ for 48 hours to obtain wheat-straw carbon sample.

2.2.2 Preparation of wheat-straw nanofibers

The preparation process of wheat-straw nano fibers is shown in Figure 1. Add different mass ratio(1:0, 9:1, 8:2, 7:3, 6:4) of polyacrylonitrile(PAN) and biomass carbon (total mass of the solute is 2.5 g) into the 25 mL N,N-dimethylformamide(DMF) at 60℃ and stir for 2 hours. Then ultrasonically disperse for 6 hours after dissolution fully to make polyacrylonitrile(PAN) and wheat-straw fully mixed. These samples are respectively recorded as PAN, PAN-C1, PAN-C2, PAN-C3 and PAN-C4. Suck the prepared solution into the syringe and put it into the push device of electrospinning apparatus for spinning. The conditions for electrospinning are: negative high pressure: 5.0KV; positive high pressure: 19.0KV; push rate: 0.15mm/min; distance between needle and receiving plate bracket: 20cm; ambient temperature: room temperature, 25℃. After spinning finished, the wheat-straw nanofibers are obtained.

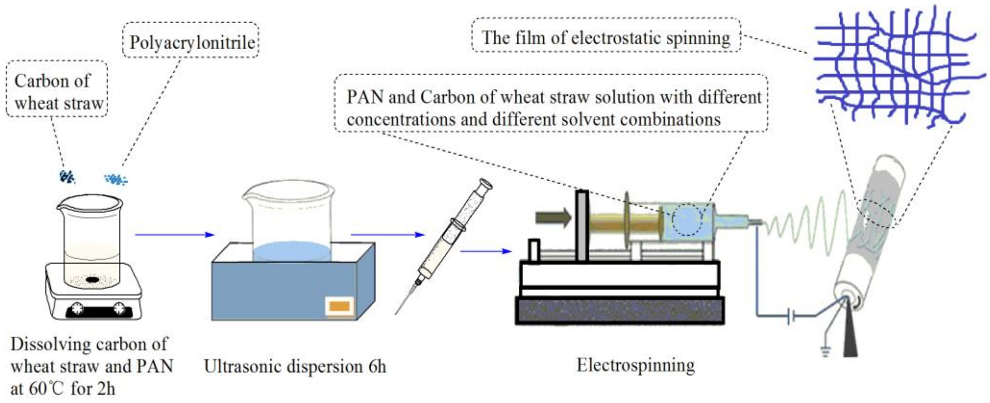


Figure 1. The preparation process of the wheat-straw nanofibers

2.2.3 Preparation of wheat-straw carbon nanofiber electrode

Put the prepared wheat-straw nanofibers into a beaker and add 2 mol/L potassium hydroxide solution[18] for activating 12 hours. Then wash several times with distilled water until the aqueous solution is neutral and dry in 60℃ for 4 hours in a vacuum drying box. Put the activated nanofibers into the muffle furnace and rise the temperature up to 280 ℃ at 1 ℃/min heating rate for preoxidation 3 hours at constant temperature[20]. After reduced to room temperature, put the nanofibers into a tube furnace, rise the temperature up to 600 °C, 700 °C and 800 °C respectively at 2 °C/min heating rate in the nitrogen atmosphere and keep for 1 hour to carbonize the nanofibers.

In order to conduct the further electrochemical performance test, mix 80% wheat-straw nano carbon fibers, 7.5% acetylene black, 7.5% conductive graphite and 5% polytetrafluoroethylene emulsion of 60 wt%[21] in a mortar, drop PTFE dispersion to prepare active electrode material. Then the mixture is grinded to paste and smeared evenly on an area of 1 cm × 1 cm of 2 cm × 1 cm nickel foam surface. Finally it is treated in a vacuum drying box at 80℃ for 12 hours[22]. The above coated samples is pressed into electrode sheet by the powder pressing machine at 10 MPa. Weigh the quality of the foamed nickel before and after coatings to calculate the quality of the active substance for evaluating the electrochemical performance of the materials.

3. RESULT AND DISCUSSION

3.1 Infrared spectra of wheat-straw carbon and the nanofibers

The infrared spectra of wheat-straw carbon and wheat-straw/PAN composite nanofibers are shown in Figure 2.

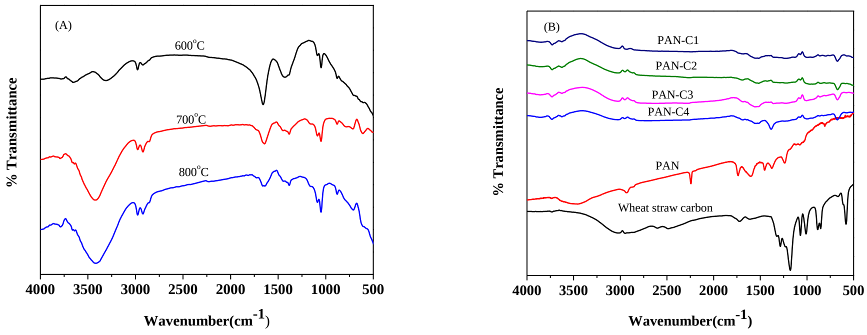


Figure 2. Infrared spectra of PAN-C1 prepared under different temperature (600℃, 700℃, 800℃)(A), and the wheat-straw carbon, PAN and the wheat-straw nanofibers with different proportions of PAN (B).

The absorption peaks at 3412 cm^{-1}, 2923 cm^{-1}, 1582 cm^{-1} and 1256 cm^{-1} are respectively assigned to -OH, -C-H, -C=C and -C-O stretching vibrations on the surface of the carbon nanofibers(Fig. 2A). The carbon nanofibers have the same absorption peaks indicates that they have the same oxygen functional groups on the surface and shows the characteristics of carbon materials. PAN-C1 obtained at 800℃ possesses the strongest peak intensity suggesting more functional groups, which is beneficial to improve the capacitance performance of sample. From Fig.2B, it is found that PAN-C1, PAN-C2, PAN-C3 and PAN-C4 contain similar characteristic peaks, indicating that they have the same oxygen containing functional groups on the surface. These peaks are obviously different from those of PAN and wheat-straw carbon.

3.2 Thermogravimetric analysis of wheat-straw carbon and the nanofibers

Take 9 to 10 mg sample for thermogravimetric analysis. The temperature is heated up to 800 ℃ in N_2 atmosphere and the heating rate is 10℃/min, the results are shown in Figure 3. In Fig. 3(a), TG curve of the wheat-straw carbon, the weight loss from 80℃ to 220℃ results from the desorption of adsorbed water on the surface, and the weight loss from 220℃ to 300℃ derives from evaporation of water in the interior. At about 300℃, the wheat-straw carbon starts to decompose. The carbonyl groups dehydrate into anhydride and some bound side chain groups are oxided to CO_2 and H_2O. Compared with the wheat-straw carbon, the composite nanofibers(PAN-C1) start to decompose at a higher temperature of 300℃ as shown in Fig. 3(b). And at 800℃, the residual mass fraction is 27.8% higher than that of the wheat-straw carbon(11.4%). Above results indicate that the composite nanofibers have a higher thermal stability.

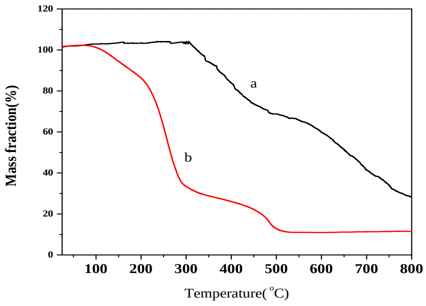


Figure 3. TGA results of the wheat-straw carbon(a) and PAN-C1 nanofibers(b)

3.3 Surface morphologies of the nanofibers

Figure 4 are respectively SEM images of PAN and PAN-C1 nanofibers before and after heating treatment. Compared with PAN fibers, the composite nanofiber surfaces are relatively more rough(Fig.4A and 4B) with fine particles attached above, indicating that the wheat-straw carbon has successfully combined with PAN. The average diameter of the precursor of PAN fibers is 805.3 nm, after carbonization it is reduced to 158.2 nm(Figure 4 A and 4C), While the average diameter of the precursor of PAN-C1 fibers is 734.8 nm, after carbonization it is reduced to 114.5nm(Figure 4B and 4D). Above results show that PAN fibers and PAN-C1 fibers have been successfully transformed into nano carbon fibers.

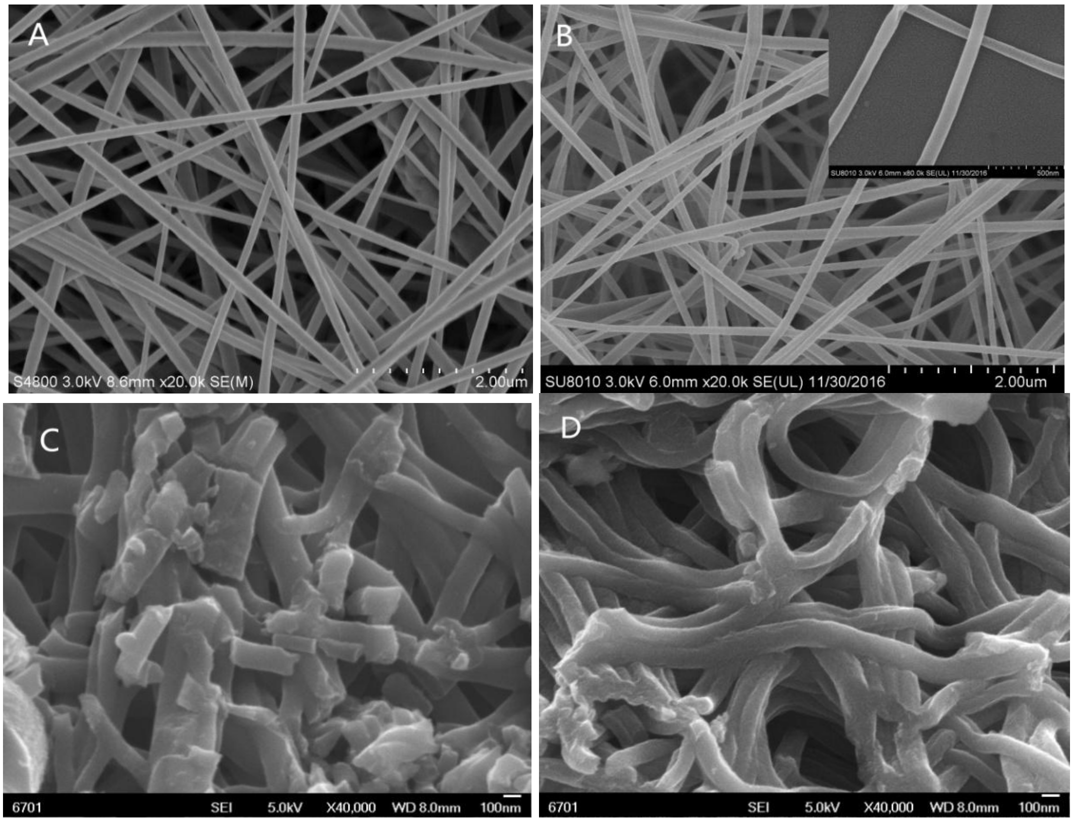
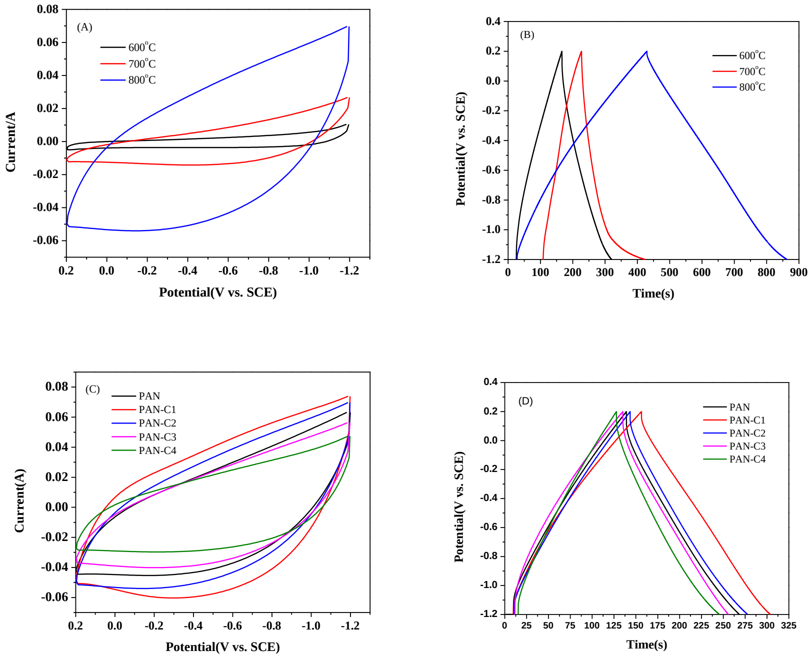


Figure 4. SEM images of PAN(A, C) and PAN-C1 nano fibers(B, D) before and after carbonization

3.4 Electrochemical properties of the wheat-straw carbon nanofibers

Cyclic voltammetry(CV), chronopotentiometry(CP) and electrochemical impedance spectroscopy(EIS) are respectively employed to evaluated the electrochemical properties of the wheat-straw carbon nanofibers in 6mol/L KOH solution.



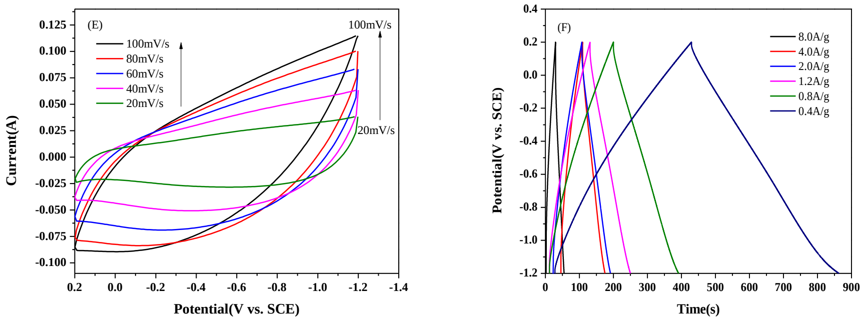


Figure 5. Electrochemical performance of wheat straw carbon fiber electrode in three electrode system. (A) and (B) CV at a 50mV/s san rate and charge-discharge curves at a current density of 0.4A/g of PAN-C1 obtained respectively under 600℃, 700℃ and 800℃; (C) and (D) CV at a 50mV/s scan rate and charge-discharge curves at a current density of 1A/g of PAN, PAN-C1, PAN-C2, PAN-C3 and PAN-C4 treated under 800℃; (E) CV curves of PAN-C1 obtained under 800℃ under different san rates(20mV/s, 40mV/s, 60mV/s, 80mV/s, 100mV/s); (F) Charge-discharge curves of PAN-C1 obtained under 800℃ at different current densities of (0.4 A/g, 0.8 A/g, 1.2A/g, 2.0 A/g, 4.0 A/g, 8.0 A/g).

Fig. 5 are respectively corresponding cyclic voltammetric and constant current charge-discharge curves.Fig. 5A and 5B show that carbonization temperature has a great effect on the electrochemical properties of the wheat-straw carbon nanofibers. In lower temperatures, the crystallization is not complete and the resulted material possesses a high resistivity, which hinders the electrolyte wetting and formation of electric double layer in potential scanning. With the carbonization temperature increasing, the specific capacitance increases and when the temperature reaches 800℃ it reaches the highest. All of CV curves are similar to rectangle and the constant current charge-discharge curves display a triangle shape, which indicates that the nanofibers have a typical double layer capacitance characteristic.(Fig. 5A-5F). Fig. 5C and 5D also show that PAN-C1 nanofiber possesses an optimal capacitance performance compared with other fibers.

The specific capacitance (C_m) of the electrode is estimated from Equation (1) [23,24]:

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

Where *I* is discharge current, *Δt* is the discharge time, *ΔV* is the voltage range and *m* is the mass of the active materials. The calculated specific capacitances of PAN, PAN-C1, PAN-C2, PAN-C3 and PAN-C4 electrodes were respectively 186.8 F/g, 211.4 F/g, 193.2 F/g, 173.2 F/g and 168.8 F/g at the current density of 1 A/g. Obviously, the capacitance performance of PAN-C1 electrode is the best, which is consistent with the test results of cyclic voltammetry. Under the same conditions, specific capacitance of the PAN carbon fibers is 186.8 F/g, only 88.4% of the PAN-C1 electrode's.

Fig. 5E shows that with the scan rate increasing, CV curves of PAN-C1 electrode gradually departs from rectangle, its capacitance performance becomes poorer. However, even at 100 mV/s, the PAN-C1 still maintains a quasi rectangle, which shows that the PAN-C1 has a good supercapacitor characteristic at high sweep speed.

When the current density increases from 0.4 A/g to 8.0 A/g, the charge-discharge curves show a good linear and symmetrical characteristic of the double layer capacitor. However, the specific capacitance decreases from 249.0 F/g to 97.1 F/g, and the capacitance retention rate is 40.0%(Fig. 5 F).

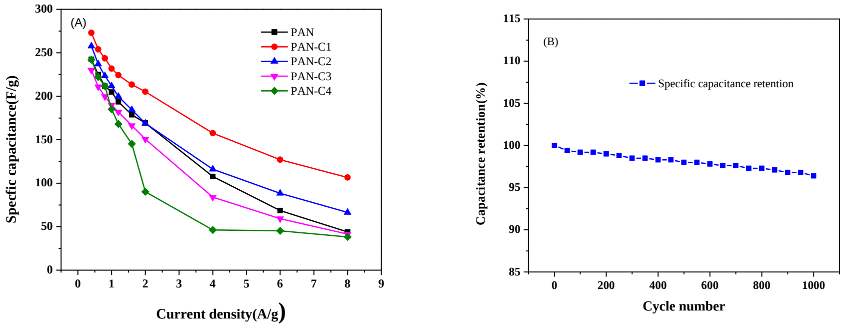


Figure 6. Specific capacitance changes of PAN, PAN-C1, PAN-C2, PAN-C3 and PAN-C4 nanofiber electrodes at different current densities(A) and specific capacitance retention rates at the current density of 2 A/g after 1000 cycles(B).

Fig. 6 shows dependence of the specific capacitance of the different nanofibers on current density and cyclic stability. Fig. 6A displays that with the current density increasing, the specific capacitance gradually reduces. The specific capacitances of the PAN-C1 electrode are the highest at different current densities. According to Eq. (1), in the current density of 2 A/g, the specific capacitance is 187.2 F/g at the first charge-discharge and 180.5 F/g over 1000 cycles, the retention rate is 96.4%, showing an excellent cyclic stability(Fig.6 B).

To evaluate applicability and practicability of the prepared supercapacitor, Table 1 lists a comparison of our results with nanofibers based supercapacitors published previously.

Table 1. Comparison of electrochemical properties of some nanofiber electrodes

Electrode materials	Specific capacitance(current density)	Specific capacitance retention(cyclic times)	Referencces
TiO_2 nanofibers	65.84F/g	90%(10000)	[25]
Polyimide based hollow carbon nanofibers	221F/g(0.2A/g)	95%(5000)	[26]
Hierarchical porous MnO_2/carbon nanofibers	228F/g(1mA/cm^2)	92%(1000)	[27]
Microporous carbon nanofibers	<180F/g(1A/g)	94%(1000)	[28]
Wheat-straw carbon nanofibers	211.4F/g(1A/g)	96.4(1000)	This work

He et al[25] prepared TiO_2 nanofiber by an electrospining technique and a post treatment with KOH and studied its capacitive property. However, even if its specific capacitance of 65.84 F/g at 1mV/s scan rate was probably the highest for reported TiO_2 electrode materials[29,30], it was relatively poor. Especially when the current density exceeded 0.5 mA/cm^2 the specific capacitance would be less than 35F/g.

Porous hollow carbon nanofibers（PHCNFs), fabricated by using styrene-acrylonitrile copolymer(SAN) solution as core and polyacrylic acid(PAA) as shell with a co-axial electrospining technique and taking polyvinyl pyrrolodone)PVP) as pore inducer additive in the shell, showed a relatively good capacitive property with specific capacitance of 221F/g at 0.2 A/g curent sensity and an excellent capacitance retention of 95% after 5000 cycles under a scan rate of 0.1V/s[26]. However, when the current densities increased to 0.4A/g and 2A/g respectively, it would decrease to about 215A/g and 205A/g which were slightly lower than the results in this work.

Lee et al.[27] prepared electrospun nanofiber(NF) webs by electrospining a solution, which contained an appropriate amount of $MnCl_2$(3 wt%) in DMF with different ratios of polyacrylonitrile(PAN)/methylmethacrylate(PMMA), into nanofiber webs. The resulted carbon nanofiber composites with hierarchical porous MnO_2 carbonized at 800℃ were used as electrode materials of supercapacitor. Their CV curves retained quasi-rectangular shape at different potential scan rates and the composite with PAN/PMMA ratio of 7:3 showed the optimal capacitive property. When the current density was $1mA/cm^2$, the highest specific capacitance was 228F/g. The supercapacitor also showed a good electrochemical stability and the specific capacitance retained 92% after 1000 cycles.

Microporous carbon nanofibers(MCNFs) synthesized by Liu et al.[28] via electrospining technique and phase separation in the presence of PVP also displayed good capacitive characteristics with specific capacitances of 200, ~189 and ~162 F/g respectively at current densities of 0.5, 1 and 2A/g and cyclic stability with a capacitance retention rate of 93% after 1000 cycles of charge and discharge.

Compared with above results, our material showed equal, or even better capacitive property. When current densities are respectively 0.4, 1 and 2A/g, the specific capacitances are 249, 211.4 and 187.2A/g and the cyclic stability is better at higher current density of 2A/g. At the same time, using wheat-straw as raw materials remarkably reduces the production cost as well.

Fig. 7 shows the electrochemical impedance spectra(EIS) of the wheat-straw carbon nanofibers in 6 mol/L potassium hydroxide solution. In the high frequency region, the semicircle diameter and Z axis real part of intercept represents the value of the impedance, including the solution resistance, resistance of carbon materials and resistance between electrode active material and collector[31]. The greater the half arc, the greater the electron transfer resistance and the worse the conductivity.

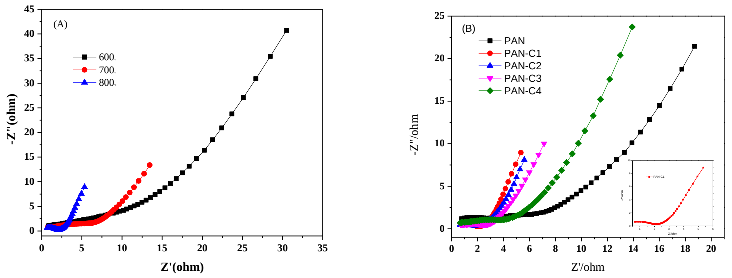


Figure 7. Electrochemical impedance spectra(EIS). (A) PAN-C1 electrode obtained under different temperatures; (B) PAN electrodes with different contents of the wheat-straw carbon

Fig. 7A shows that with the treatment temperature increasing, the electron transfer resistance decreases and the conductivity increases. Fig.7B displays that when the wheat-straw carbon is introduced into PAN matrix, Z axis real part of intercept becomes shorter and the slope of the low frequency region increases, which indicates that addition of the wheat-straw carbon increases the charge transfer energy and improves electrochemical properties of the nanofiber electrode. However, with the content of the wheat-straw carbon in the composite nanofibers increasing, the impedance between the electrolyte and the nanofiber electrode rises, PAN-C1 nanofiber electrode shows the optimal conductivity.

4. CONCLUSIONS

With wheat straw and polyacrylonitrile(PAN) as raw materials a novel wheat-straw carbon nanofiber electrode material for supercapacitors is prepared by an electrospinning method. When PAN is doped 10% wheat-straw carbon, the resulted composite nanofiber electrode material shows a highest specific capacitance of 249.0F/g at the current density of 0.4A/g. The prepared supercapacitor has a good cyclic stabiity and the specific capacitance only reduces 3.6% after 1000 cycles at a current density of 2A/g. Using waste biomass resources to prepare the valuable energy materials not only improves utilization efficiency but also solves effectively environmental pollution problems.

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