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Preparation and Electrochemical Performance of Activated Composite Carbon Nanofibers Using Extraction Residue from Direct Coal Liquefaction Residue

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Abstract: Organic carbon extracted from direct coal liquefaction residue (DLCR) is an ideal precursor for the preparation of carbon materials. However, investigations into the utilization of the extraction residue (ER) are rarely reported. In this work, ER from DCLR was pretreated with H_2O_2 to afford oxidized extraction residue (OER). Then, the OER was mixed with polyacrylonitrile (PAN) in *N*,*N*-dimethylformamide for the preparation of composite carbon nanofibers by electrospinning. With adding 80 wt.% OER, the composite carbon nanofibers still demonstrate a clear fiber profile and smooth surface under a scanning electron microscope, indicating that the OER has good solubility with PAN in *N*,*N*-dimethylformamide. The electrochemical performance characterization of the activated composite carbon nanofiber shows that the P-OER60-AC (activated composite carbon nanofibers prepared with 60 wt.% of OER and 40 wt.% of PAN) has a better electrochemical performance with a specific capacitance of 97 F/g at 0.5 A/g, as compared to the others. Additionally, the P-OER80-AC (activated composite carbon nanofibers prepared with 80 wt.% of OER and 20 wt.% of PAN) is also considerable for the perspective of coal-based solid waste treatment and utilization.

Keywords: direct coal liquefaction residue; extraction residue; electrospinning; composite carbon nanofibers; electrochemical performance

1. Introduction

Direct coal liquefaction residue (DCLR), a byproduct from the direct coal liquefaction process [1], is a typical coal-based solid waste but is also valuable carbon resource. DCLR is rich in condensed and heteroatom-containing aromatic structures and is thereby a superior raw material for acquiring valuable polycyclic aromatic hydrocarbons (PAHs) [2,3]. But pyrogenic PAHs, generated through the incomplete combustion of coal and its byproducts (including DCLR) [4,5], can pose higher risks to human health and environmental ecology. Moreover, heteroatom-containing PAHs, especially nitrogen [6] and sulfur [7], in coal and its byproducts are considered as precursors of environmental contaminators (NOx and SOx) when using coal and its byproducts as fuels [8,9], including acid rain, photochemical smog, the greenhouse effect, and ozone layer depletion.

Additionally, a high content of mineral matter in DCLR is also great challenge for DCLR's clean utilization. The mineral matter is released into the air as fine and ultrafine particles during DCLR conversion. PAHs and some metallic micro-particles are adsorbed onto the particles, thereby causing a higher risk of lung cancer [10]. Reports have shown that the PAHs in coal smoke are a major carcinogen contributing to a high lung cancer risk, since high concentrations of carcinogenic PAHs have been found in the emission particles



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). from coal combustion associated with the highest lung cancer risk [11], and lung cancer risks were shown to decrease by around 50% after stove improvement and venting the coal smoke outdoors [12–14]. Therefore, the clean and valuable utilization of DCLR is essential.

The extract from DCLR was successfully applied in the preparation of carbon fibers by arc-jet plasma [15] and the melt-spinning approach [16], as it has a good solubility in organic solvents [17]. Moreover, owing to the good solubility of organic carbons in tetrahydrofuran and polyacrylonitrile in dimethylformamide, a DCLR-based carbon nanofiber film was also prepared as electrodes for supercapacitors [18] and in lithium-/potassium-ion batteries by electrospinning [19]. Electrospinning carbon nanofiber film has drawn great attention as a method to produce flexible and freestanding supercapacitor electrodes due to its advantages of high surface area, light weight, structural controllability, and convenience in fabrication [20,21]. However, extraction residue (ER) from DCLR has failed to attract researchers' interests, and it has thereby always been treated as waste and useless matter. Both of the structural features and valuable utilization of ER have rarely been reported.

In this work, in order to show the potential utilization of ER from DCLR, the structural features of the ER were explored by Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectrometry (XPS), and thermogravimetric analysis (TG). The ER was pretreated with H_2O_2 and then mixed with polyacrylonitrile to produce composite carbon nanofibers by electrospinning. The morphology and electrochemical performance of the composite carbon nanofibers were investigated.

2. Materials and Methods

2.1. Sample Preparation

The DCLR was obtained by liquefying Shenmu–Fugu subbituminous coal at 455 °C under 19 MPa of hydrogen in a pilot-scale direct coal liquefication unit operated by Shenhua Group Corporation Ltd., Baotou City, Inner Mongolia, China. It was pulverized to <74 μ m followed by desiccation in a vacuum at 80 °C for 24 h prior to use. The DCLR was extracted exhaustibly using an isometric acetone/carbon disulfide mixture under ultrasonic irradiation and then in a Soxhlet extractor, where the insoluble portion that remained in the Soxhlet extractor was collected and tableted as the ER. All the reagents used in the experiments were of analytical grade, and all the organic solvents were distilled with a Büchi R-300 rotary evaporator prior to use.

2.2. Direct Analysis of the ER

The occurrence forms of heteroatoms on the surface of the ER were measured on a ThermoFisher ESCALAB 250Xi XPS device with monochromatic Al K α radiation operated at 150 W and with pass energies of the whole spectra of 0 keV~5 keV. The energy calibration was conducted using the containment carbon (C 1s = 284.8 eV) [22]. For obtaining the fraction of various functional groups containing O, N, or S, the C 1s, N 1s, and S 2p spectra obtained from the XPS analysis were curve-resolved using a 20%Lorentzian–80%Gaussian line shape by the "XPS PeakFit" software (V4.1). The ER was mixed with potassium bromide (KBr) powder and pressed into tablet. The tablet was then directly analyzed with a Nicolet Magna IR-560 FTIR spectrometer. The FTIR spectra were recorded by collecting 64 scans at a resolution of 4 cm⁻¹ operating in the reflectance mode with measuring regions of 4000~400 cm⁻¹. A Mettler Toledo thermogravimetric analyzer was employed to analyze the ER with heating rate of 10 °C/min from 30 °C to 900 °C and by holding at 110 °C for 10 min.

2.3. Preparation and Characterization of Composite Carbon Nanofibers

Pretreatment of ER: A total of 10.00 g of dried ER with 100 mL of H_2O_2 solution (30% by volume) [23,24] was placed in a 500 mL round-bottomed flask and then oxidized at 60 °C for 3 h. An oxidized ER (OER) sample was obtained by washing the sample with deionized water to neutral and then drying at 60 °C for 24 h and storing it in a sealed bottle after 200 mesh sieves.

Samples of 0.50 g of PAN with certain masses of OER (0.33 g, 0.50 g, 0.75 g, 1.17 g, 2.00 g) were ultrasonically dissolved in 5 mL of *N*,*N*-dimethylformamide and magnetically stirred at 70 °C for 4 h to form a uniform black viscous liquid. The nonwoven composite carbon nanofibers (i.e., composite carbon nanofiber precursors) were obtained by electrospinning at the following electrospinning parameters: injection velocity of 0.12 mm/min, collector rotation speed of 30 r/min, distance between tip and collector of 10 cm, positive high pressure of 12 kV, and negative high pressure of 3 kV. The samples were named P-OER40, P-OER50, P-OER60, P-OER70, and P-OER80.

The composite carbon nanofiber precursors were collected from the aluminum foil and then placed in tempered glass container with a 40 wt.% HNO₃ solution at room temperature for 1 h (the composite carbon nanofiber precursors were completely immersed in the HNO₃ solution). Then, the composite carbon nanofiber precursors were washed repeatedly with deionized water to neutral and dried in a drying oven at 60 °C for 12 h. The treated composite carbon nanofiber precursors were then placed in an air atmosphere at heating rates of 5 °C/min up to 120 °C and held for 2 h, 2 °C/min up to 160 °C and held for 2 h, 2 °C/min up to 230 °C and held for 2 h, and 2 °C/min up to 280 °C and held for 2 h. The stabilized composite carbon nanofiber precursors were named P-OER40-280, P-OER50-280, P-OER60-280, P-OER70-280, and P-OER80-280.

Finally, the composite carbon nanofibers were obtained by carbonizing with a heating rate of 5 °C/min up to 850 °C. The samples were named P-OER40-C, P-OER50-C, P-OER60-C, P-OER70-C, and P-OER80-C. The surfaces of the composite carbon nanofiber precursors were characterized by a Nova Nano SEM450 ultrasonic field emission scanning electron microscope (SEM) provided by FEI. Thermogravimetric analysis of the stabilized composite carbon nanofiber precursors was carried out using a German synchronous thermogravimetric analyzer. In the experiment, high-purity N₂ was selected as the carrier gas with gas flow rate of 50 mL/min, a temperature of 30 °C~900 °C, and a heating rate of 3 °C/min. The carbon contribution ratio of OER and PAN to the composite carbon nanofibers was also calculated.

2.4. Preparation and Characterization of Activated Composite Carbon Nanofibers

The composite carbon nanofibers were placed in a 40% KOH solution for 24 h at 80 °C. After drying, they were placed in a tubular resistance furnace in a N₂ atmosphere with a heating rate of 3 °C/min up to 800 °C, held at a constant temperature for 2 h, taken out after natural cooling to room temperature, repeatedly washed with deionized water to neutral, and dried to a constant weight to obtain the activated composite carbon nanofibers. The samples were named P-OER40-AC, P-OER50-AC, P-OER60-AC, P-OER70-AC, and P-OER80-AC.

The characterization of the surface area and aperture measurement of the samples were conducted using an ASAP-2460 physical adsorption instrument produced by the McMuriatic Company in the United States [25,26]. A total of 0.1 g of sample was degassed in a vacuum environment at 300 °C for 12 h to remove air, water, and other impurities adsorbed onto the surface of the sample. The test was performed using liquid nitrogen at a temperature of -196 °C, and the relative pressure (air pressure/saturated vapor pressure) of the adsorption isotherm test ranged from 0.01 to 0.995. The BET multi-molecular layer adsorption theory was used to calculate the specific surface area. The *t*-plot method was used to characterize the micropore structure, specific surface area, and pore volume. The BJH method was used to characterize the mesoporous structure.

The electrochemical performance system used in this experiment was a three-electrode test system. A pressed platy electrode was used as the working electrode, a platinized platinum electrode of 1 cm \times 1 cm was used as the opposite electrode, and a Ag/AgCl electrode was used as the reference electrode. The prepared 6 mol/L KOH solution was selected as the electrolyte solution. After the sample preparation, the electrochemical performance of the carbon-based electrode was tested by the CHI660D electrochemical workstation of Shanghai Chenhua Instrument Co., Ltd. (Shanghai, China).

Cyclic voltammetry (CV) is mainly used to show the capacitance characteristics of carbon-based electrode materials and the reversible degree of the electrode reaction. The potential range was selected as $-1.0 \text{ V} \sim -0.3 \text{ V}$, and the scanning rate was selected as 10 mV/s, 20 mV/s, 30 mV/s, 50 mV/s, 100 mV/s, and 200 mV/s. Constant-current charging–discharging (GCD) was used in the carbon electrode material in this research and in the parameter calculation of the electrochemical nature of the charge and discharge performance. The voltage range was set as $-1.0 \text{ V} \sim 0 \text{ V}$, and the current density was selected as 1 A/g, 2 A/g, 4 A/g, 10 A/g, and 20 A/g. The specific capacitance, energy density, and power density were calculated by the equation $C = (I \times \Delta t)/(m \times \Delta U)$, where *C* is specific capacity, *I* is the circuit current, Δt is the discharge time, *m* is working electrode's active material (carbon-based materials), and ΔU is the quality of the pressure drop for the process. The impedance method is an important method used to measure the internal impedance of electrodes. During the measurement of this experiment, the amplitude of AC signal selected was 5 mV, and the frequency interval was $0.01 \sim 1 \times 10^5 \text{ Hz}$.

3. Results and Discussion

3.1. Structural Features of ER by Direct Analysis

As displayed in Figure 1a, the XPS analysis shows that C was the dominant element of the ER, with a relative content of 83.51%, followed by O, S, Ca, Si, and N with relative contents of 12.15%, 1.19%, 1.16%, 1.08%, and 0.91%, respectively. As shown in Figure 1b, the XPS spectra of the C 1s, N 1s, and S 2p were divided into several peaks. As listed in Table 1, according to the related assignments [22], carbon was mainly present as aliphatic carbon and aromatic carbon, with molar contents of 56.22% and 35.48%, respectively. Oxygen-containing species existed in the forms of C–O, COO–, and C=O, with a total molar content of 7.3% in the carbon.



Figure 1. (a) XPS survey spectrum and (b) C 1s, N 1s, and S 2p spectra with their fitting curves of ER, (c) FTIR spectrum of ER, and (d) thermogravimetric and derivative thermogravimetry curve of ER.

The existing forms of nitrogen decreased in the following order: pyrrolic > pyridinic > quaternary > amino. More than 80% of the nitrogen existed in the aromatic rings. Both organic and inorganic sulfur were identified in the ER, with molar contents of 44.87% and 55.13%, respectively. Sulfate was the most abundant, with a relative content of 48.68%,

which was a result from the CLR and raw coal. Organic-sulfur-containing species existed in the forms of aliphatic sulfur, aromatic sulfur, sulfoxide, and sulfone, in which sulfone was the most abundant, followed by aromatic sulfur, sulfoxide, and aliphatic sulfur. The higher molar content of sulfone and sulfoxide could have been a result of the oxidation of aromatic and aliphatic sulfur species on the DCLR surface or as a result of coal weathering during outdoor storage.

Elemental Peak	Functionality	Binding Energy (eV)	Molar Content (%)	
C 1s	Aliphatic carbon	284.60	56.22	
	Aromatic carbon	285.11	35.48	
	C-O	286.36	5.65	
	COO-	287.91	0.10	
	C=O	289.45	2.55	
N 1s	Pyridinic	398.50	23.60	
	Amino	399.13	6.94	
	Pyrrolic	400.25	57.75	
	Quaternary	401.97	11.72	
	Pyrite	161.50	6.45	
	Aliphatic sulfur	162.61	5.48	
S 2n	Aromatic sulfur	163.77	12.16	
52p	Sulfoxide	164.98	10.53	
	Sulfone	168.99	16.71	
	Sulfate	169.90	48.68	

Table 1. Distributions of carbon, nitrogen, and sulfur forms in ER by XPS analysis.

As shown in Figure 1c, typical absorbances for coal-related matter were present around 2932 cm⁻¹, 2856 cm⁻¹, 1601 cm⁻¹, 1449 cm⁻¹, 855 cm⁻¹, 825 cm⁻¹, and 753 cm⁻¹. The bands located at the 2932 cm⁻¹, 2856 cm⁻¹, and 1449 cm⁻¹ positions are typical for aliphatic compounds in coal-related resources, i.e., C–H present in methyl and methylene. The absorbance at 1601 cm⁻¹ was assigned to C=C stretching vibrations present in aromatic rings. The bands at around 855 cm⁻¹, 825 cm⁻¹, and 753 cm⁻¹ imply that there were substituted aromatic rings [27,28] in the ER. The peak at 1091 cm⁻¹ was attributed to a Si–O band of silicate from CLR. The strong peaks near 536 cm⁻¹ and 467 cm⁻¹ were due to mineral matter from the raw coal. A catalyst would also contribute to the peaks, including iron sulfate, ferrous sulfate, and pyrite [29], which is consistent with the S 2p spectrum from the XPS analysis and also its elemental analysis [30]. C–O, COO–, and C=O also existed in the ER, as shown by the absorbance bands around 1704 cm⁻¹, 1219 cm⁻¹, and 1101 cm⁻¹, which were in agreement with the XPS analysis.

As depicted in Figure 1d, the pyrolysis of the ER was conducted from 30 °C to 900 °C, with a total weight loss ratio of 34.58 wt.%. The pyrolysis process mainly occurred over 650 °C and had the highest DTG at 730 °C. The main weight loss was caused by pyrolysis of the macromolecular skeleton, the thermal decomposition of mineral matter, and the polymerization of semi-coke.

3.2. Morphology and Stability of Composite Carbon Nanofiber Precursors

As presented in Figure 2, the color of the nonwoven (composite carbon nanofiber precursors) turned from light gray to dark grey as the mass ratio of OER increased. The color of the composite carbon nanofiber precursors was closer to the OER's color as the mass ratio of OER increased. The colors of the composite carbon nanofiber precursors mainly reflected the OER's color. Moreover, the exterior color of the composite carbon nanofiber precursors was homogeneous, indicating that the OER and PAN were uniformly dispersed.

As demonstrated in Figure 3, the composite carbon nanofiber precursors had a clear morphology, a smooth surface, and a uniform diameter, indicating that the OER had good solubility with PAN in the spinning solution. Additionally, the fiber diameter did not



increase significantly as the mass ratio of OER increased, implying that the OER and PAN had good consistency during the electrospinning.

Figure 2. Pictures of composite carbon nanofiber precursors with different OER mass ratios.



Figure 3. SEM images of composite carbon nanofiber precursors with different OER mass ratios.

As displayed in Figure 4a, all of the samples had no obvious thermogravimetric behavior under 400 °C. The precipitation of water and small volatile components was mainly accompanied by a weak pyrolysis behavior. Thereby, the stabilized composite carbon nanofiber precursors had a certain weight loss behavior in this temperature range (around 150 °C). Additionally, the weight loss rate was low, which was mainly caused by some aromatic compounds with a low molecular mass. Pyrolysis mainly occurred in the temperature range from 400 °C to 800 °C. All the six samples had obvious weight loss at about 400 °C and reached the highest weight loss rate at about 680 °C, especially for the pure PAN with the highest weight loss rate of more than 80 wt.%. Pyrolysis of the macromolecular skeleton, the thermal decomposition of inorganic minerals, and the condensation of semi-coke mainly occurred over 650 °C [31,32]. The mass loss ratio implies that the macromolecular organic matter skeleton structure and inorganic minerals were the main components of the OER, while few low- and medium-molecular-mass organic compounds existed. Compared to the thermogravimetric analysis of the ER shown in Figure 1d, the P-OER80-280 sample had a similar pyrolysis behavior and total mass loss. These results provide evidence for the successful preparation of the nonwoven carbon nanofibers.



Figure 4. (a) Thermogravimetric analysis of composite carbon nanofiber precursors, (b) N_2 adsorptiondesorption isothermal curves, and (c) pore diameter distributions of activated composite carbon nanofibers.

To evaluate the carbon contribution of OER and PAN to the composite carbon nanofibers, the carbon contribution ratio was calculated by the following equations.

$$CCR_{PAN} = 100\% \times M_{residual \ carbon-PAN} / TM_{residual \ carbon}$$

$CCR_{OER} = 100\% \times M_{residual\ carbon-OER} / (TM_{residual\ carbon} - M_{PAN-residual\ carbon})$

where M_{PAN} is the mass of PAN, M_{OER} is the mass of OER, R_{PAN} is the ratio of PAN, R_{OER} is the ratio of OER, $TM_{residual \ carbon}$ is the total mass of residual carbon, $TY_{residual \ carbon}$ is the total yield of residual carbon, $M_{residual \ carbon-PAN}$ is the mass of residual carbon from PAN, $M_{residual \ carbon-OER}$ is the mass of residual carbon from OER, CCR_{PAN} is the carbon contribution ratio of PAN, and CCR_{OER} is the carbon contribution ratio of OER.

As listed in Table 2, the mass of residual carbon from PAN ($M_{residual\ carbon\ PAN}$) in each of the carbon nanofibers was 0.25 g, which was based on the total mass of residual carbon from pure PAN. The mass of residual carbon from OER ($M_{residual\ carbon\ OER}$) in the composite carbon nanofibers was calculated by the difference. Compared to the composite carbon nanofiber precursors, the pure PAN had a lower stability and a higher mass loss, as the total yield of residual carbon ($TY_{residual\ carbon}$) from PAN was only 50.27 wt.%. The total yield of residual carbon ($TY_{residual\ carbon}$) of the P-OER40-C, P-OER50-C, P-OER60-C, P-OER70-C, and P-OER80-C samples was 60.18 wt.%, 62.35 wt.%, 65.85 wt.%, 67.10 wt.%, and 68.49 wt.%, respectively. The carbon contribution ratio of OER (CCR_{OER}) for the composite carbon nanofibers increased as the mass ratio of OER increased, resulting in values of 49.86 wt.%, 59.69 wt.%, 69.46 wt.%, 77.53 wt.%, and 85.32 wt.% of the carbon contribution ratio for the composite carbon nanofibers.

Table 2. Carbon contribution ratios of OER and PAN to different carbon nanofibers.

	Carbon Nanofibers with Different Mass Ratio of OER					
Items –	PAN-C	P-OER40-C	P-OER50-C	P-OER60-C	P-OER70-C	P-OER80-C
M_{PAN}/g	0.50	0.50	0.50	0.50	0.50	0.50
M_{OER}/g	0.00	0.33	0.50	0.75	1.17	2.00
R _{PAN} /wt.%	100	60	50	40	30	20
R_{OER} /wt.%	0	40	50	60	70	80
$TM_{residual \ carbon}/g$	0.25	0.50	0.62	0.82	1.12	1.71
M _{residual carbon-PAN} /g	0.25	0.25	0.25	0.25	0.25	0.25
$M_{residual carbon-OER}/g$	0	0.25	0.37	0.57	0.87	1.46
CCR _{PAN} /wt.%	100	50.14	40.31	30.54	22.47	14.68
CCR _{OER} /wt.%	0	49.86	59.69	69.46	77.53	85.32
TY _{residual carbon} /wt.%	50.27	60.18	62.35	65.85	67.10	68.49

3.3. Structural and Surface Features of Activated Composite Carbon Nanofibers

As shown by the absorption and desorption curve depicted in Figure 4b, the adsorption capacity surged at low pressure, which is in line with the characteristics of a type *I* curve. The sample surface was dominated by a microporous structure, while a relatively gentle hysteresis loop appeared on the desorption curve, indicating that there were few mesoporous structures in the samples.

As shown in Figure 4c and Table 3, the mesoporous pore size of the sample was mainly distributed around 4 nm, and the microporous pore size mainly ranged from 0.5 nm to 0.6 nm. The microporous and mesoporous pores were generated by nitrogen carbonization and KOH activation. OH⁻ reacts with carbon atoms at high temperatures, thereby causing carbon atoms to be oxidized and released as a gas, leaving micropores on the surface of carbon fibers [33]. The micropores were caused by inorganic matter from the OER, as the pore-forming process would have been impeded by the inorganic matter. The decrease in the samples' specific surface area would also support this conclusion, as would the increase in the mass ratio of OER in the composite carbon nanofiber precursors.

Samples	$S_{BET} a (m^2/g)$	V _t ^b (cm ³ /g)	V _{mic} ^c (cm ³ /g)	$V_{mic}/V_t^{\ d}$ (%)	D _{ap} ^e (nm)
P-OER40-AC	276	0.181	0.113	73	2.32
P-OER50-AC	184	0.126	0.075	75	2.40
P-OER60-AC	155	0.116	0.061	69	2.58
P-OER70-AC	139	0.133	0.048	72	3.08
P-OER80-AC	93	0.083	0.035	50	2.93

Table 3. Specific surface area and pore structure of activated composite carbon nanofibers.

^a Specific surface area by BET, ^b total pore volume at $P/P_0 = 0.99$, ^c pore volume of micropore by *t*-plot, ^d ratio of micropore, ^e average pore size.

3.4. Electrochemical Performance of the Activated Composite Carbon Nanofibers

As displayed in Figure 5, the activated composite carbon nanofibers presented good characteristics of double-layer capacitance, and the CV curve shape became more rectangular as the scanning rate decreased [34]. The activated composite carbon nanofibers still presented good double-layer capacitance characteristics at a scan rate of 80 mV/s. However, obvious deformation of the shape of the CV curve occurred at a scanning rate of 100 mV/s, indicating that the scanning rate increased more than the current density at this scanning rate. As shown in Figure 6, the activated composite carbon nanofibers showed typical double-layer capacitance characteristics due to the good symmetry of the charge–discharge curve and the approximate isosceles triangle shape of the curve.

As presented in Figures 5 and 6, the mass ratio of OER had no obvious effect on the shape of the CV and charge-discharge curves, but it had significant effect on the specific capacitances. The P-OER60-AC sample had better double-layer capacitance characteristics and a better specific capacitance than the others. Even both the total yield of residual carbon of the composite carbon nanofibers and the carbon contribution ratio of OER increased as the mass ratio of OER increased, which was more beneficial for the morphology and stability of the composite carbon nanofibers. This is because the amount of inorganic matter from ER was also increased, and this would be adverse for the electrochemical properties.

As exhibited in Figure 7, the curve slope changed and the capacitance value decreased at a scan rate of 100 mV/s, indicating that the electrochemical performance of the sample became unstable. As shown in Figure 5, a superposition occurred at the CV curves of 100 mV/s and 80 mV/s, which is consistent with the results shown in Figure 7. The curve shape was slightly convergent as the scanning speed increased at a scanning rate of over 100 mV/s, implying that the rate capability decreased at a scanning rate over 100 mV/s. Thereby, the increase in the scanning rate was greater than the current density. However, the current density and the double-layer capacitance were fair when the mass ratio of OER was increased to 80 wt.%.



Figure 5. CV curves of (**a**) P-OER40-AC, (**b**) P-OER50-AC, (**c**) P-OER60-AC, (**d**) P-OER70-AC, and (**e**) P-OER80-AC samples.



Figure 6. GCD curves of (**a**) P-OER40-AC, (**b**) P-OER50-AC, (**c**) P-OER60-AC, (**d**) P-OER70-AC, and (**e**) P-OER80-AC samples.



Figure 7. Scan–current density curves of (a) P-OER40-AC, (b) P-OER50-AC, (c) P-OER60-AC, (d) P-OER70-AC, and (e) P-OER80-AC samples.

The alternating-current impedances of the activated composite carbon nanofibers were investigated and are presented in Figure 8. Compared to the others, the ESR value of the P-OER60-AC samples was the smallest, and the EIS curve was an arc radius in the high-frequency region, reflecting that the interface resistance between the electrode and the electrolyte was the smallest. This also demonstrates that the P-OER60-AC sample had little ion transport resistance and could easily form a double layer [35]. The curve of the P-OER60-AC sample is shown by a vertical slashed line in the low-frequency region, indicating that the charge–discharge process was diffusion-controlled. The mass transfer rate of an electrode material affects the slope of the slant, i.e., the higher the slope, the better the capacitive performance. Therefore, the impedance slope of samples increased in the low-frequency region as follows: P-OER70-AC < P-OER50-AC < P-OER40-AC < P-OER80-AC < P-OER60-AC, indicating the mass transfer velocity of the electrode materials had an increasing trend.



Figure 8. Impedance of P-OER40-AC, P-OER50-AC, P-OER60-AC, P-OER70-AC, and P-OER80-AC samples.

The mass ratio of OER had a certain effect on the internal resistance of the electrode, which was mainly caused by inorganic matter from the CLR. However, the electrochemical performance of activated composite carbon nanofibers depends on their synthetic characterization. Therefore, the P-OER60-AC sample would be the preferred activated composite carbon nanofiber in this study.

4. Conclusions

This work carried out a novel approach for the efficient utilization of coal-based solid waste to prepare composite carbon materials using electrospinning. The composite carbon nanofibers precursors have good spinnability and morphology. OER has a better stability than PAN in the carbonization process, resulting in a higher carbon contribution ratio to the composite carbon nanofibers. The activated composite carbon nanofibers show better electrochemical performances, with a specific capacitance of 97 F/g at 0.5 A/g with 60 wt.% of OER and 40 wt.% of PAN in the mixture. It is noteworthy that this research provides a feasible way for the preparation of composite carbon nanofibers with OER as the main material and with PAN as the skeleton. However, the electrochemical performances of the activated composite carbon nanofibers would be affected by the remaining minerals, which need more treatment. Additionally, the expanded application of composite carbon nanofibers in other fields still needs further investigation.

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