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Preparation of interconnected carbon nanofibers as electrodes for supercapacitors

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ABSTRACT

The interconnected carbon nanofibers were prepared by an electrospinning technique using a polymer solution composed of polyacrylonitrile (PAN), poly(acrylonitrile-co-butadiene (PAN-co-PB) copolymer, and N,N-dimethylformamide. Post-treatment including stabilization at 250 °C and carbonization at 800 °C converted electrospun fibers to bonded carbon nanofibers. The formation of interconnected carbon nanofibers was attributed to the decomposition of PB, which reduced the viscosity of nanofibers and caused the fusion of connecting points. As a result, the conductive pathways developed, leading to an increase in both the electrical conductivity and microcrystallite size. Electrochemical measurements revealed that the specific capacitance of the 90:10 PAN/PAN-co-PB derived carbon nanofibers was 170.2 F/g, which was about 24% higher than that of the neat PAN-derived carbon nanofibers. Furthermore, the fibers showed good cycling stability of energy storage with the retention ratio of 100% after 2000 cycles. Our results corroborated the advantage of these interconnected nanofibers.

1. Introduction

Supercapacitors are considered as prospective energy storage system because they have many advantages, such as high power density, short charging and discharging time, long cycle life, and broad working temperature, when compared to the conventional capacitors and secondary batteries [1,2]. Since the electrochemical performance of supercapacitors is mainly governed by the electrode materials, the development of materials with high capacitance and power density is an immanent task to achieve the industrial desire.

The electrochemical performance of electrodes relies on the high surface area, average pore diameter, surface functionalities to ensure the fast oxidation-reduction reaction, and high electrical conductivity. Currently, considerable effort has been put to develop carbonaceous materials for the use as electrodes because they have advantages of abundance, good electrical conductivity, low cost, non-toxicity, high chemical stability, and simplicity of preparation [3,4]. Among them, electrospun carbon nanofibers, which have large surface area and porosity, seem to be an excellent candidate for electrode materials. However, the use of carbon nanofibers for supercapacitors is still restricted to the low power and energy density. To improve the electrochemical properties of carbon nanofibers, the modification of carbon nanofibers is carried out. For example, Kim et al. [5] utilized the electrospinning technique to prepare nonwoven carbon webs. It was obtained that the increased activation time during carbonization facilitated the development of microporous structural fibers. This in turn increased the surface area of fibers and improved the specific capacitance. Carbon nanofibers with a microporous structure could also be generated by the addition of polymethylhydrosiloxane (PMHS) in PAN precursor solution [6]. High activation temperature could also increase the activation yield, leading to the increases in both the surface area and electrical conductivity of fibers [7–9]. On the contrary, Ra et al. [10] found that the amount of N-containing groups on fibers decreased when the activation temperature increased. In such a way, the increased electrical double layer and decreased pseudocapacitive contributions cancelled out. As a result, the specific capacitance only slightly depended on the activation temperature. Niu et al. [11] modified the fiber morphology by the addition of polyvinylpyrrolidone (PVP) in precursor solution. The PVP partially melted at early stage of pyrolysis. This facilitated the fiber connection, resulting in a bonded fibrous structure. Although the change in the surface area of these interconnected fibers was not significant, the increased specific capacitance of the fibers was obtained. Tran and Kalra [12] incorporated Nafion in precursor solution to prepare porous carbon nanofibers. Due to its rigidity and the

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high decomposition temperature, Nafion could prevent fibers from shrinking and collapsing during stabilization, promoting the formation of a more-defined pore structure. The specific capacitance showed a ten-time increase when compared to the neat carbon nanofibers.

Another approach to improve the electrochemical performance of electrospun carbon nanofibers is to introduce other electroactive materials. Ju et al. [13] prepared randomly dispersed ruthenium nanoparticles in carbon nanofibers. The composite fibers showed a great enhancement on the specific capacitance, which was associated to the synergistic effect of electric double layer capacitance as a result of the expansion of the average pore diameter as well as the pseudo-capacitance by the well-dispersed ruthenium particles. Similarly, zinc chloride was incorporated into precursor solution to prepare electrospun fibers [14]. Due to the increased conductivity of the precursor solution upon the addition of zinc chloride, the electrospun fibers showed reduced fiber diameter. Meanwhile, zinc chloride accelerated the oxidative stabilization rate, which effectively created suitable pores on the fiber surface during pyrolysis. As a result, enhanced specific capacitance of fibers was obtained. The addition of carbon nanotubes in carbon nanofibers was also reported to efficiently increase both the pore size and the electrical conductivity of fibers [15,16]. In single-walled carbon nanotube containing nanofibers, the single layer of nanotubes would be damaged under CO_2 activation, providing pathways for CO_2 diffusion. On the contrary, the multiple layers in multi-walled carbon nanotube containing nanofibers remained intact under CO_2 activation, which inhibited CO_2 diffusion. As a result, single-walled carbon nanotube containing nanofibers showed both higher specific surface area and larger pore size, leading to better electrical performance [17]. The properties of the carbon nanotube-containing fibers could be further improved by tailoring polypyrrole on the tube surface. The polypyrrole formed small conducting granular particles at the interface between nanofibers and nanotubes, which promoted the formation of conducting bridges connecting the polypyrrole conducting domains and the effective percolation. Tai et al. [18] prepared a flexible carbon nanofiber/graphene composite paper and the paper exhibited 24% enhancement on the specific capacitance when compared to the neat carbon nanofiber paper. Similar to Tai's work, Zhou and Wu [19] reported the synthesis of graphene-beaded carbon nanofibers via electrospinning. The carbon nanofibers acted as frameworks to bridge the graphene nanosheets and prevented the nanosheets from severe swelling and shrinking during the cycling process. The specific capacitance of the graphene-beaded carbon nanofibers reached to 263.7 F/g at a discharge current density of 100 mA/g and the retention ratio was 86.9% after 2000 cycles.

Although electrospinning is an efficient method to prepare polymer and composite nanofibers, the nonwoven structures during electrochemistry-associated processes may cause low charge-transfer efficiency due to the insufficient fiber-fiber contact, leading to large contact resistance and prolonged charge-transfer through the electrode [20]. The lack of inter-fiber connection may also reduce the pore stability. In this work, we demonstrate a strategy to prepare interconnected nanofibers by electrospinning. The web-type structure of the nanofibers is considered to provide good intra- and inter-fiber conductivity, which is particularly important as an electrode material for supercapacitors. It has to be pointed out that the concept of preparing interconnected carbon nanofibers has never been reported by other researchers. Our results reveal that the interconnected carbon nanofibers exhibited significantly improved electrical conductivity and electrochemical performances when compared to those of the uniform separated nanofibers. These results clearly suggest the potential of the interconnected carbon nanofibers for the use as electrodes for supercapacitors.

2. Experimental Section

2.1. Materials

Polyacrylonitrile (PAN, MW = 150000 g/mole) and poly (acrylonitrile-*co*-butadiene) (PAN-co-PB, acrylonitrile content of 8 ~ 12 wt%, MW = 3800 g/mole) were purchased from Sigma-Aldrich. N,N-dimethyl formamide (DMF) was provided by J. T. Baker.

2.2. Preparation of carbon nanofibers

A solution of 7 wt% PAN/PAN-co-PB with various compositions in DMF was continuously stirred for 24 h at room temperature. The electrospinning was conducted in a homemade setup equipped with a DC power supply, manufactured by You-Shang Technical Corporation. Initially, the polymer solution was placed in a 10 mL glass syringe with a stainless needle tip, which was connected to a positive high-voltage power supply. The negative terminal was connected to an aluminum foil collector. The collector was placed vertically at a horizontal distance of 15 cm from the tip. During electrospinning, the flow rate of the polymer solution was fixed at 0.7 mL/h and the applied voltage was 15 kV. The as-spun nanofibers were then placed in a tubular quartz furnace and the pyrolysis was performed firstly at 250 °C for 4 h in air, followed by carbonization at 800 °C for 1 h in nitrogen.

2.3. Characterization

A JEOL JSM-6700F scanning electron microscope (SEM) was used to observe the general features of the fibers. The fibers were sputter-coated with platinum for imaging by use of a JEOL JFC-1600 coater. The accelerating voltage for SEM measurement was 10 kV. The average fiber diameter was determined by analyzing at least 50 fibers per sample for statistical purposes. Thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer TGA-7. Experiments were carried out from room temperature to 800 °C at 10 °C/min in nitrogen. X-ray diffraction (XRD) analysis of the carbon nanofibers with various blend compositions was performed using a Rigaku RINT-2000 diffractometer coupled to a source of filtered CuK_α radiation. Data were collected in the angle scan from 10 to 60° with a scan rate of 4°/min. Raman scattering was conducted on carbon nanofibers in the backscattering configuration using a Thermo Scientific Thermo DXR Raman microscope (Thermo Fisher Scientific). The wavelength of the laser beam was 532 nm. The specific surface area of the carbonized nanofibers was determined by the Brunauer–Emmett–Teller (BET) method (ASAP2020, Micromeritics). The measurements were carried out using N_2 adsorption at 77 K. The electrical conductivity (σ) of the electrospun carbon nanofibers was measured using the four-probe method. The σ value was calculated according to

$$\sigma = \frac{l}{Rw} \quad (1)$$

where l is the distance between electrodes, R is the electrical resistance, and w is the thickness of the specimen.

The electrochemical properties of the carbon nanofibers were investigated in a conventional Teflon electrochemistry cell with a three-electrode cell and a potentiostat (CHI 627D, CH instruments) operated at room temperature. For the measurements, Ag/AgCl was used as reference electrode in 2 M KOH and a platinum foil was the counter electrode. The carbon nanofiber film was cut into 1 cm × 1 cm square and then put on a nickel foil for a working electrode. Due to the web-type structure of the electrospun fibers, the addition of binders is not required and this prevents from the degrading of supercapacitor performance [21]. The cyclic