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Electrospun fibrous electrodes with tunable microstructure made of polyaniline/multi-walled carbon nanotube suspension for all-solid-state supercapacitors

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ABSTRACT

Electrospinning technique was used to prepare high performance fibrous electrodes with tunable microstructure for all-solid-state electrochemical supercapacitor. Symmetrically sandwiched supercapacitors consisting of flexible electrospun polyaniline (PANI)/multi-walled carbon nanotube (MWCNT) electrodes and polyvinyl alcohol (PVA)/sulfuric acid (H_2SO_4) gel electrolyte were assembled. Tunable microstructure of the fibrous electrode was obtained by changing the electrospinning parameters including the collector–needle distance (CND) and the suspension flow rate (SFR). Results show that, higher CND combining with lower SFR can result in a smaller average diameter of the electrospun fibers and hence improve the electrode performance. When the CND changes from 80 to 140 mm, the average fiber diameter will decrease from 2.89 to 1.21 μm, and the specific surface area of the electrode can increase from 57 to 83 $m^2 \cdot g^{-1}$. The corresponding specific capacitance of the electrospun electrode will therefore increase from 129.5 to 180 $F \cdot g^{-1}$, leading to a synchronous improvement of the energy density of the supercapacitor from 18 to 25 $Wh \cdot kg^{-1}$. On the other hand, the supercapacitors using fibrous electrodes in this work also show good rate capability and cycling stability. Using the electrode with an average fiber diameter of 1.21 μm, the specific capacitances can maintain 131 $F \cdot g^{-1}$ at a current density of 4 $A \cdot g^{-1}$, which is 73% of the specific capacitance of the same sample at a current density of 0.5 $A \cdot g^{-1}$. And the specific capacitance of the electrode can retain 89% after 1500 charge/discharge cycles.

1. Introduction

Recently, there are increasing demands for renewable energy sources due to the rapid depletion of fossil fuels. High performance energy-storage devices, as an important part in the applications of renewable energy, have attracted more and more attentions from scientific communities [1–3]. Electrochemical supercapacitor has long been considered as an attractive energy-storage device because of its advantages such as high power density, fast charging/discharging rate, long cycle life and high reliability [4].

The electrode with high specific surface area and proper porosity has significant impacts on the supercapacitor performance [5,6]. However, the micro–nano structure of the electrode is quite difficult to be accurately controlled using traditional preparation techniques such as brush coating, vacuum filtration and electrochemical deposition [7,8]. Electrospinning is a facile, cost-effective and scalable method for preparation of micro–nano fibers with large specific surface area, and has been successfully applied to produce fibrous electrode for electrochemical supercapacitors [9–12].

PANI is a promising conductive polymer electrode material for supercapacitors and has been widely studied because of its ease of synthesis, good environmental stability, high conductivity and theoretical specific capacitance [13,14]. However, the practical supercapacitor applications of PANI as electrode material were still subject to several serious challenges such as its large volume change and poor cycling stability in the charging/discharging process. Fortunately, these issues can be addressed by incorporating PANI with carbon-based nano-materials, which can achieve the synergistic performances in electrochemical double-layer capacitors and pseudo capacitors [15]. Therefore, nanostructured carbon materials with large specific surface area and high conductivity had been used as materials to generate composited electrode with both long cycle life and high performance [12,14–17]. However, comparing with numerous studies already done on the PANI

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composite electrodes made by traditional methods, much less is known about the performance of electrospun PANI/multi-walled carbon nanotube (MWCNT) fibrous electrodes. Moreover, little research concerning the effects of electrospun microstructure on the electrode performance has been reported so far.

In this work, electrospinning technique was adopted to prepare fibrous electrodes using PANI/MWCNT compound suspension, and microstructure of the electrodes was adjusted by changing the electrospinning parameters including the collector–needle distance (CND) and the suspension flow rate (SFR). Finally, effects of the electrospun microstructure on the electrode performance were comparatively studied and discussed.

2. Experimental

2.1. Materials

The hydrochloric acid doped, emeraldine base PANI compound was synthesized via in situ polymerization, polyethylene oxide (PEO, Mw = 1,000,000) and 10-camphorsulfonic acid (HCSA) used as co-spinning agents were obtained from Aladdin Chemical Reagent. The MWCNT has an average diameter of 10 nm, length between 0.1 and 1 μm, and a purity of 95%. The electrospinning suspension was prepared by dissolving PANI (0.1 g) in chloroform (10 ml), followed by the addition of camphorsulfonic acid (0.129 g) to the PANI solution. The suspension was then stirred for 12 h at room temperature using a magnetic stirrer, and then filtered through a filter paper to remove any particulate matter. Thereafter, MWCNT (0.1 g) was added to the solution and ultrasonically stirred for 2 h. Finally, PEO (0.15 g) was added to the PANI/MWCNT compound, and again magnetically stirred for 12 h before electrospinning. It should be noted that, in a PANI/MWCNT composited electrode, the addition of the MWCNT can effectively increase the specific surface area and electrical conductivity of the electrode [16,18,19]. However, when considering the dispersion of MWCNTs in the PANI-chloroform solution and the electrical conductivity of the electrospun electrode, there is an optimum mass ratio of MWCNT and PANI in the electrospinning suspension, which is close to 1:1, as reported in [20]. The research of this manuscript is mainly focused on the effects of different fibrous structures on the performance of the electrospun electrodes, and this optimum mass ratio (0.1 g MWCNT: 0.1 g PANI) was directly used in our experiments to facilitate the discussion of the effects of electrospun structures based on the same material component and proportion. The effects of different PANI/MWCNT mass ratio will be included in our follow-up study.

2.2. Electrospinning

The schematic diagram of the electrospinning apparatus is shown in Fig. 1. To fabricate the fibrous electrodes, the electrospinning suspension was filled into a 2.5 ml syringe with a tip that has a 0.4 mm inner diameter. In this work, the electrospinning experiments were divided into four groups and denoted as 1#, 2#, 3# and 4# according to different electrospinning parameters as listed in Table 1. In each experiment, the CND and SFR were simultaneously changed, and then electrospinning voltage was appropriately adjusted at constant CND and SFR to provide sufficient electrospinning electric field. The electrospun fibers were received by a carbon paper which also acts as current collector of the supercapacitor. Each electrospinning process was conducted for about 6 h to obtain fibrous electrode with enough thickness. In our experiments, the effective area of the carbon paper for receiving the electrospun fibers is $1.0 \times 1.0\ cm^2$, and the final mass loading of the active materials on this effective area is $3\ mg\ cm^{-2}$, which was determined by a drying–weighing method.

2.3. Supercapacitor assembly and characterization

The carbon papers with electrospun fibrous electrode were dried at room temperature. Then two electrodes were face-to-face stacked together, separated by a polytetrafluoroethylene (PTFE) porous membrane impregnated with PVA/H_2SO_4 gel, to form a symmetrically sandwiched, all-solid-state electrochemical supercapacitor, as shown in Fig. 2. In this study, the morphology of the fibrous electrode was characterized with scanning electron

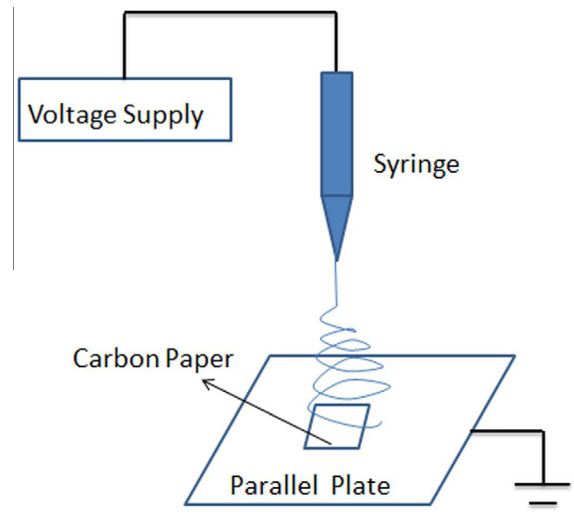

Fig. 1. Schematic diagram of the electrospinning apparatus.

Table 1
Electrospinning parameters in different experiments.

Experiment No.	CND (mm)	SFR (μL/min)	Electrospinning voltage (kV)
1#	80	3.5	6.12
2#	100	3	7.02
3#	120	2	8.00
4#	140	1	9.01

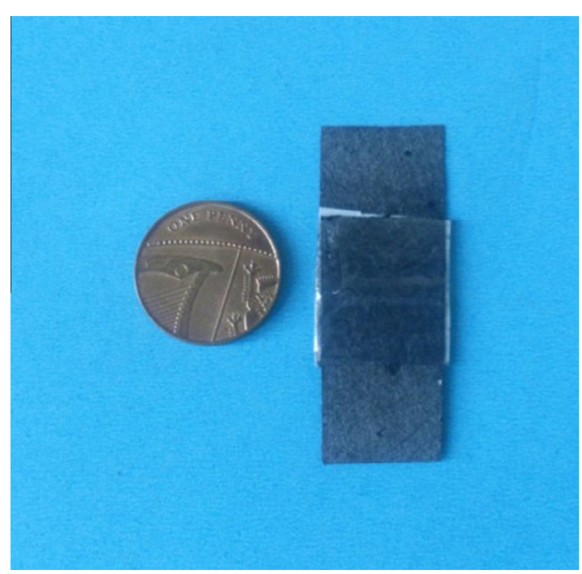

Fig. 2. As-prepared supercapacitor.