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Full paper

All-climate aqueous fiber-shaped supercapacitors with record areal energy density and high safety

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ABSTRACT

Flexible fiber-shaped supercapacitors (FSSs) are promising energy storage candidates for wearable electronics. However, most of reported FSSs are operated at room temperature and used the toxic flammable organic electrolyte or corrosive strong acid or base which may have safety hazards especially for wearable textiles directly sticking on the human skin at harsh environmental temperatures. Here we reported a new kind of aqueous symmetric FSSs with high safety and record high areal energy density at wide operating temperature ranging from − 60 °C (14.2 μW h cm^{-2}) to 75 °C (22.9 μW h cm^{-2}) based on aqueous LiCl-PVA based gel electrolyte and core-shell nanocrystalline polymer fiber electrode. The fabricated aqueous FSSs demonstrate high flexibility, high areal/volumetric energy density and stable cycle life at different operating temperatures, showing the potential application in all-climate wearable electronics.

1. Introduction

Wearable and smart textiles have been rapidly developed and presented promising applications in portable electronic devices [1–5]. Fiber-shaped supercapacitors (FSSs) have the merits of small volume, high flexibility and easy assembly into various designed structures that attract increasing interest and are considered as one of the promising energy storage candidates for wearable textiles [6–10]. Compared to those of supercapacitors and batteries with conventional two-dimensional configurations, one-dimensional FSSs have much lower specific energy that limited their practical applications [11,12]. Most of efforts have been made to fabricate high energy densities FSSs at room temperature by designing high-capacitance materials with high conductivity and high ion-accessible surface area [13–15] and fabricating asymmetric configurations with wide operating-voltage nonaqueous (organic solvent or ionic liquid) and aqueous electrolytes [16–18].

Despite tremendous progress has been made for the FSSs, there still remain enormous challenges including low energy density, high cost, degradation in extremely cold/hot zones and leakage safety of liquid electrolyte [19,20]. The reported FSSs mostly are based on the highly toxic and flammable organic electrolyte (acetonitrile with high volatility and low flaming point) [20–23] or high viscosity and cost ionic liquids [23–26] or concentrated acid (H_2SO_4, H_3PO_4) or base (NaOH) solvent [27–30], which can cause severe safety risks. Especially for flexible and wearable textiles directly sticking on the human skin, the potential safety risk is higher and worse when these FSSs are bended or twisted repeatedly during the practical using at wide temperature range. Meanwhile, up to date, most of the reported FSSs focus on room temperature performances [31–34], which may not work under extremely operating temperatures that could not meet the requirement of wide human being territory from the frigid winter period (temperatures below −20 °C) to the hot equatorial regions (temperatures high than 40 °C) [35]. The performance of the supercapacitors may deteriorate at extreme temperatures which results in issues such as capacitance decay, internal resistance increase, cycle life degradation and thermal runaway triggered by thermal stress from internal heat generation, which severely limit the practical application [36–38]. However, only few studies have been reported regarding the performance of fiber-shaped supercapacitors at different operating temperatures, as summarized in Table S1 and S2. To the best of our knowledge, flexible aqueous FSSs with large areal energy density and high safety at extremely operating temperature lower than 0 °C and higher than 80 °C have not been reported so far. Generally, there are a few technical challenges for realizing high-performance FSSs for extreme temperature applications, mainly including as follows [19,26]: (1) The reaction kinetics become sluggish due to the decreased conductivity of the electrode and electrolyte at low temperatures which lead to poor high-rate capability. Thus, the active electrode materials should be designed with high conductivity to counteract this negative effect; (2) The viscosity of the electrolytes increases rapidly with the decreased temperature which

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results in decelerated ion diffusion, thus large ion-accessible surface is needed to alleviate the negative temperature effect; (3) The electrode materials and binders may decompose and peel off from current collector under intense reaction at high temperature. To solve this issue, the FSSs with synergistic electrode materials and suitable electrolyte should be developed to maintain high electrochemical performances at wide operating temperatures.

Herein, we designed a new kind of all-climate aqueous symmetric fiber-shaped supercapacitors with record high areal energy density at wide operating temperature ranging from − 60 to 75 °C and high safety by combination of aqueous LiCl-PVA based gel polymer electrolyte and core-shell nanocrystalline polymer fiber electrode. The inner core of the fiber consists of conductive polymer and a small amount of amorphous RuO_2 which provide high pseudocapacitance. The outer shell consists of nanocrystalline conductive polymer which not only provides pseudocapacitance, but also functions as current collector and buffer layer that suppress the structural pulverization and prevent the possible side-reaction of the RuO_2 under extreme operating temperature. The assembled FSSs exhibited an excellent flexibility and high energy densities over a wide temperature range from − 60 to 75 °C. It displayed ultrahigh energy density of 22.5 μW h cm^{-2} with wide potential window of 1.5 V at 25 °C and also could effectively cycle for 5000 cycles at − 60 °C with a capacitance retention of 97.2% and energy density of 14.2 μW h cm^{-2}. To the best of our knowledge, such high areal energy density of symmetric FSSs with aqueous gel electrolyte at − 60 °C has not been reported yet. At wide temperature from − 60 to 75 °C, high flexibility and excellent electrochemical properties were maintained under bending 2000 times. In addition, it also could work as efficient power supply for light-emitting diodes (LEDs) at different operating temperatures.

2. Experimental section

2.1. Materials

Clevios PH1000 (PEDOT:PSS) (1.0 wt%) was provided by HC Starck, Inc. $RuCl_3{\cdot}3H_2O$ (AR), Ethylene glycol (EG) (AR), isopropyl alcohol (IPA) (AR), and ethanol (AR) were provided by Sigma-Aldrich. Ethanol (AR), LiCl (AR), PVA 1788 (Mw 75,000–78,000) (AR), $CaCl_2$ (AR) and concentrated H_2SO_4 (≥ 98%) were provided by Kelong Chemical Reagent Company.

2.2. Preparation RuO_2 nanoparticle

First, 1 mol L^{-1} NaOH solution was added into 100 mL 0.1 mol L^{-1} $RuCl_3{\cdot}3H_2O$ solution with vigorous stirring for 1 h at room temperature. The mixed solution was continues stirred 12 h, and then washed and centrifuged with distilled water several times to remove residual NaCl salts. The precipitate was obtained by freeze-dry after centrifugation. Last, the as-preparation sample was heated 12 h at 150 °C.

2.3. Wet-spinning of fibers

The concentrated PEDOT:PSS (2.0 wt%) was prepared by evaporated half the water at 50 °C. RuO_2 NPs were dispersed in the ethanol with concentration of ~ 50 mg mL^{-1}. The mixed solution of RuO_2 and PEDOT:PSS (1:6 wt%) was obtained by a magnetic stirrer for two hours. The prepared mixture solution was transferred into a 2 mL syringe and spun into a coagulation bath though a metal needle with an inner diameter of 260 μm. The extruded velocity of the solution was controlled between 0.25 and 1 mL min^{-1} by using a syringe pump. The coagulating bath was ethanol: water (3:1 v/v) solution with 3 wt% $CaCl_2$. After coagulation for 10 min, the composite fibers were treated by EG solvent for 10 s to remove the PSS followed by deionized water washing. Subsequently the fibers were treated by IPA solvent for 10 s to remove the residual water followed by deionized water washing. It was wound on a PTFE rod before drying in a vacuum oven at 120 °C. Then, PEDOT:PSS-RuO_2 fibers were dipped into PEDOT:PSS solution to coat a thin protected layer PEDOT:PSS. After that, it was coagulated in the coagulation bath followed by the same treatment with EG and IPA for the PEDOT:PSS-RuO_2 @PEDOT:PSS fibers. Finally, PEDOT: PSS-RuO_2@ PEDOT:PSS fibers were immersed into concentrated H_2SO_4 for 10 min to remove insulated PSS. Then, the PEDOTS-RuO_2@PEDOTS fibers were sufficiently washed by deionized water and dried at 120 °C for 10 min to remove residual water. For comparison, PEDOT:PSS-RuO_2 fibers were immersed into concentrated H_2SO_4 for 10 min to remove insulated PSS (PEDOTS-RuO_2).

2.4. Preparation of PVA solid electrolyte

15 g LiCl was added into the 100 g deionized water by magnetic stirring for 10 min. Then 10 g PVA1788 dissolved in the above solution at 90 °C and was kept stirring for 1 h to obtain LiCl-PVA (PVA: LiCl: H_2O = 1: 1.5: 10 wt.) gel electrolyte. For comparison, H_3PO_4-PVA gel (PVA: H_3PO_4: H_2O = 1: 1.5: 10 wt.), H_2SO_4-PVA gel (PVA: H_2SO_4: H_2O = 1: 1.5: 10 wt.), PVA solution (PVA: H_2O = 1: 10 wt.), and LiCl solution (LiCl: H_2O = 1.5:10 wt.) were also prepared.

2.5. Construction of supercapacitors

Fiber-shaped supercapacitors (FSSs) were constructed with two fibers in parallel at an interval of approximately 1 mm and covered with PVA gel electrolyte in the surface. Both ends of the fibers were fixed to the PET film using conductive tapes. For another FSSs, two fibers paralleled side by side were wrapped on substrate with covering LiCl-PVA gel electrolyte using a stepper motor.

2.6. Characterization and electrochemical measurement

Scanning electron microscopy (SEM, Carl Zeiss SMT Pte Ltd., Ultra 55) and transmission electron micrographs (TEM, Zeiss Libra 200FE) were utilized to study the surface morphologies and crystal phase structures of the composite fibers. The crystal phase structures of fibers was tested by X-ray diffractometer (XRD, Bruker D2 Phaser) using Cu Kα radiation (λ = 1.5418 Å) operating with 30 kV and 10 mA. X-ray photoelectron (XPS) spectra were acquired with an Axis Ultra DLD (Shimadzu-Kratos Co.). Infrared spectrum was measured using a Spectrum One Nicolet-5700 Fourier transform infrared (FT-IR) spectroscopy at scanning range from 4000 to 400 cm^{-1}. Raman spectra were implemented on a customized Raman microscope equipped with Pixis-100BR CCD (Princeton Instrument, US) at the range of 100–4000 cm^{-1}, Acton SP-2500i spectrograph, He-Ne laser (14 mW) was used as excitation source (Princeton Instrument, US). The strain-stress curves of the single fiber were measured by using single fiber electronic tensile strength tester (LLY-06E). Thermal gravimetric analysis (TGA) were tested at the oxygen atmosphere from room temperature to 800 °C at a rate of 10 °C min^{-1} by the Mettler TGA1 SF. A VSP-300 (Bio-Logic SAS, France). Electrochemical workstation was conducted to measure the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). EIS was recorded in a frequency range of 0.1 Hz to 100 kHz at an open-circuit voltage with an oscillation amplitude of 5 mV. The specific conductivity of the fibers was tested by the electrochemical workstation by two-probe method. Arbin battery testing equipment (BT-2000, Arbin) was used to test the Galvanostatic charge-discharge (GCD) curves. The constant temperature magnetic stirring tank (PSL-1810, EYELA) was used to conduct the low temperature measurements from 0 to − 60 °C. Differential scanning calorimetry (DSC) was measured on a Mettler DSC 3 + .

2.7. Differential scanning calorimetry measurement

Electrolyte (15–20 mg) was sealed in an aluminum pan and then