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Novel high-performance asymmetric supercapacitors based on nickel-cobalt composite and PPy for flexible and wearable energy storage

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HIGHLIGHTS

- Acid-pretreated yarn can substantially support active materials to exhibit excellent electrochemical performance.
- Asymmetric SCs exhibited a high electrochemical performance as compared to recently reported fiber-shaped SCs.
- The SCs are also highly flexible and stable to be directly sewn into textile fabric for wearable energy storage.
- The results demonstrate the flexible SCs are promising power sources for wearable applications.

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ABSTRACT

Wearable fiber-shaped supercapacitor (SC) is a kind of one-dimensional flexible devices that can be directly knitted or sewn into various kinds of textile soft-substrate for wearable energy storage. Herein, acid-pretreated stainless steel yarn (SSY) has been developed to support electrodeposition of active materials of nickel/cobalt composite and polypyrrole (PPy) as the positive and negative electrodes, respectively. The asymmetric all-solid-state supercapacitors (AASs) showed both high electrochemical properties and excellent mechanical flexibility under various degrees of deformation. The highest volumetric capacitance reached 14.69 F cm^{-3} at the current density of 25 mA cm^{-3}, and the maximum energy density was 3.83 mWh·cm^{-3} (0.032 mWh·cm^{-2}) at a power density of 18.75 mW cm^{-3} (0.284 mW cm^{-2}). The AASs were highly flexible and durable for directly being sewn into textile fabrics, and exhibited a good electrochemical stability under 6000 charging/discharging cycles. This work uses the common materials and facile methods to fabricate the flexible and wearable AASs with enhanced electrochemical properties, showing a decent way in developing flexible SC devices.

1. Introduction

Smart textiles and the derived products are becoming increasingly popular in recent years [1]. To satisfy the power demands, flexible energy storage devices in a wide range of forms are under investigations, such as the flexible lithium-ion batteries, supercapacitors (SCs), solar cells, etc [2–10]. In particular, the flexible 1-D fiber-shaped SCs, bearing good flexibility, high efficiency, small size, and light weight, have exhibited great potential in using for flexible energy storage [1,11–15], and the use of polymeric yarns [13], carbon fibers [16], and metallic yarns [17,18] has been commonly reported in recent studies. Currently, the performances of the fiber-shape SCs are not yet satisfying the need of demand. For example, the common cotton yarns based SCs usually showed unstable and low electrochemical performance due to the poor conductivity [19,20], while some metallic yarns having inherent advantages in conductivity suffered from the lower flexibility. Thus, it is crucially important to develop flexible and wearable fiber-shaped substrate with both excellent conductivity and flexibility [19,21].

Over the past years, carbon-based materials, conductive polymers and transition metal oxides(TMOs)/sulfides(TMSs)/phosphides(TMPs) have been widely investigated as the three main materials for SCs. For the carbonaceous materials, like carbon fibers (CF), carbon nanotubes (CNTs), the reduced graphene oxides (rGO), etc., they were largely studied as electrodes for electrical double-layered capacitors (EDLCs) that are based on the electrostatic charge accumulations, because of their light weight, good conductivity, large specific surface area, etc. [22–25], but the main flaws such as the low specific capacitance restricted their further uses [26]. By contrast, TMOs (RuO_2, Fe_2O_3, NiO, Co_3O_4, MnO_2, and V_2O_5) and conductive polymers (PPy, PANI, PEDOT) demonstrated remarkable electrochemical properties, owing to the fast faradic reversible redoxs [27,28]. In particular, NiO and Co_3O_4 have

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been reported to possess the theoretical specific capacitances of nearly 3500 F g^{-1} [29]. In most cases, NiO, Co_3O_4 and their composites were synthesized in forms of nanorods, nanowires, nanograsses and nanoneedles, etc. by a hydrothermal technique [30–33], but it has been indicated that only limited amount of the electroactive materials could be loaded on the electrodes, which is actually far from satisfaction to meet the industrially-acceptable demands [19,21,34–36].

The asymmetric configuration for SCs has received an increasing attention as it can enlarge the device voltage windows and finally achieve enhanced energy density [18]. An asymmetric SC is usually made up of two different types of electrodes, such as a pseudocapacitive electrode and an EDLC type electrode. Currently, most of the reported work used carbon-based materials as the negative electrode for offering more power source [9,14,18,35]. However, the EDLC typed materials will degrade the SC performance due to the inherent low specific capacitance, as compared to the faradic pseudocapacitive materials. Therefore, it is more desirable to use the composite negative materials with high pseudocapacitive property as the negative electrode to fully improve the performance of the device.

Therefore, this study aims to develop a novel kind of high-performance and wearable fiber-shaped asymmetric all-solid-state supercapacitors that are highly flexible, stable and durable to be directly sewn into textile fabric for wearable energy storage. We developed a nickel and cobalt oxides coated SSY (NS) as positive electrode and PPy coated SSY (PS) as negative electrode by electrodeposition. The high flexibility and excellent mechanical stability offer outstanding performance in electrochemical and cyclic deformation tests. Compared with the recently reported fiber-shaped supercapacitors [14,20,37–47], our all-solid-state yarn supercapacitors exhibits a higher electrochemical performance with a high energy density of 3.83 mWh·cm^{-3} (0.032 mWh·cm^{-2}) at a power density of 18.75 mW cm^{-3} (0.284 mW cm^{-2}), and a high volumetric capacitance of 14.69 F cm^{-3} at the current density of 25 mA cm^{-3}, under an operating voltage window of 1.5 V. The wearable supercapacitors also showed a good electrochemical stability with 6000 charging/discharging cycles. As a demonstration, the as-prepared AASs were directly sewn into a common textile fabric for powering LED.

2. Experimental

2.1. Materials and apparatus

Chemicals of KOH, H_2SO_4, $NaClO_4$, HCl, HNO_3, $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, polyvinyl alcohol (PVA), pyrrole, and sodium dodecyl benzene sulfonate (SDBS) are all analytical grade. SSYs were purchased from Bekinox, with the model AISI 316L. The deionized (DI) water was produced from a desktop BENCHTOP Unique-TypeImanufactured by Xiamen RSJ Scientific Instruments Co., ltd., China.

The electrochemical workstation instrument model is ZIVE SP1, capable of completing DC and impedance characterization of various electrochemical applications. The ZIVE SP1 has a control range of ± 10 V@1Amp and a wide current range from 1A to 100 nA.

2.2. Preparation of NS and PS

2.2.1. Pretreatment of SSY

A 7-cm long SSY sample was immersed in the 6 M HCl@HNO_3 (Volume ratio, 3:1) solution for 15–30 min, followed by the rinsing of ethanol and DI water. The pretreated SSYs were then stored and dried in the oven at 60 °C for 20 min.

2.2.2. The electrodeposition of NS and PS

The electrodeposition was performed in a standard three-electrode system at the room temperature (25 ± 1 °C). During the process, a pretreated SSY served as the working electrode, while a piece of platinum plate and a saturated calomel electrode (SCE) worked as the counter electrode and the reference electrode, respectively. The aqueous electrolyte (Ni/Co molar concentration ratio of 1:1) consists of 0.05 M $Ni(NO_3)_2{\cdot}6H_2O$, 0.05 M $Co(NO_3)_2{\cdot}6H_2O$ and 0.05% (Weight ratio) SDBS. The electrodepositing process lasted for 500 s at a current of -4 mA cm^{-2} (vs. SCE). The resultant products were carefully rinsed for several times by DI water and dried in air before an annealing process at 350 °C for 2.5 h. The muffle furnace was set to a ramping temperature of 2 °C per minute. For comparison, preparations of NS electrodes with different Ni/Co molar concentration ratios (1:2, 1:3, and 2:1) were performed.

The PS electrode was similarly fabricated by the above-mentioned preparation for NS electrode, but the aqueous electrolyte was replaced by a solution of 0.2 M $NaClO_4$ and 5% pyrrole monomer. The electrodeposition was performed at a current density of 4 mA cm^{-2} for 250s, 500s and 750s.

2.3. Material characterization and electrochemical measurements

To characterize the phase of the material precisely, pieces of NS electrodes were put into a strong ultrasonic bath for collecting sample powders. The crystal structures of the nickel and cobalt mixture were examined by the XRD (Cu target, Ka, $\lambda = 0.15406$ nm) with a Bruker D8 Advance X-ray diffractometer. The surface morphologies of the electrodes were measured by an EDS detector equipped scanning electron microscopy (SEM: TESCAN VEGA3) and a transmission electron microscope (TEM: Jeol JEM-2011). The Raman spectra of the PS electrode were recorded using a micro-Raman spectroscope (JY-HR800) with the laser emitting at 532 nm. The electrochemical measurements were carried out at room temperature in a three-electrode electrochemical cell with a 3 M KOH aqueous solution as the electrolyte. The as-prepared NS acted as the working electrode, a piece of platinum plate acted as the counter electrode, and a SCE was the reference electrode. The cyclic voltammetry (CV) curves and galvanostatic charge and discharge (GCD) curves, and the electrochemical impedance spectroscopy (EIS) were measured in the electrochemical cell. Volumetric capacitances derived from GCD curves were calculated by the below equation:

$$C = I{\cdot}\Delta t\ /U{\cdot}V \tag{1}$$

where C, I, U, Δt, and V are the volumetric capacitance (F·cm^{-3}), the discharge current (A), the voltage window excludes the IR drop (U), the discharging duration (s), and the volume of the NS electrode (cm^3), respectively.

The energy density (E) and power density (P) of the device were derived from the equations:

$$E = \int I{\cdot}U(t)\ dt\ /\ (V{\cdot}3600) \tag{2}$$

$$P = E/(\Delta t{\cdot}3600) \tag{3}$$

where I, U, Δt, and V are the discharge current (A), the voltage window (U), the discharging time (s), and the volume of the device, respectively.

2.4. Fabrication of asymmetric all-solid-state SCs

Firstly, the PVA-KOH gel electrolyte was prepared by a modified technique [32,48]. 8.4 g KOH was dissolved in 50 ml DI water at room temperature, while 5 g PVA was then added in the beaker under vigorous stirring at 85–90 °C for 2–5 h. Both the positive NS and negative PS electrodes were carefully coated with a thin layer of the PVA/KOH electrolyte and dried at room temperature for 1 h before the assembly. The asymmetric all-solid-state SC was then assembled by wrapping a PS negative electrode on the as-prepared NS electrode in conjunction with the PVA-KOH as both electrolyte and separator. The electrochemical performances of the as-prepared SC were examined by the above electrochemical workstation. To balance the charges of an AAS, the